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Biodegradation of phenol and 2-chlorophenol using a fill-and-draw-reactor

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ABSTRACT

Title of Thesis : Biodegradation of Phenol and 2-Chlorophenol Using a Fill-and-Draw Reactor

Chi-Chun Tsai , Master of Science, 1986

Thesis directed by : Dr. Gordon A. Lewandowski
Associate Professor of
Chemical Engineering

The biological degradation of phenol and 2-chlorophenol was studied at room temperature in a microprocesser controlled fill-and-draw reactor using activated sludge from the Passaic Valley Sewerage Commissioners wastewater treatment plant (Newark, New Jersey). The reactor was cycled through four unit processes: fill, react, settle, and draw. Different cycle times were tested, and the system response was characterized by dissolved oxygen measurements and substrate analysis (by gas chromatography).

With inhibitory substrates, such as those tested, this reactor had much more flexibility, and was therefore much easier to operate, than a standard continuous flow reactor.

Biodegradation of Phenol and 2-Chlorophenol Using a Fill-and-Draw Reactor

By

Chi-Chun Tsai

Thesis is submitted to the faculty of the Graduate school of the New Jersey Institute of Technology in partial fulfillment of the requirements for the degree of Master of Science in

Chemical Engineering
1986

APPROVAL SHEET

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I. INTRODUCTION

The performance of many processes and operations can be improved appreciably by controlled unsteady-state operations (periodic processes) [1,2]. Studies concerning periodic operation have been carried out for adsorption, ion exchange, particle separation, countercurrent flow multistage separation, and maximum product yield. In many cases it has been shown that processes operated periodically demonstrate marked increases in performance relative to conventional steady continuous flow operations.

In the field of wastewater treatment, continuous-flow systems have dominated the technology, especially in biological waste treatment. Although fill-and-draw reactors have been around since the early 1900's, they have never gained wide spread acceptance. This was primarily due to a lack of automated equipment capable of controlling inflow and outflow, a lack of aeration equipment that would resist plugging during start/stop operation, the additional labor costs associated with maintenance and supervision, and the perceived advantages of continuous processes. However, with recent advances in process control, the daily operation of a semibatch plant can be greatly simplified. Furthermore,

like all semibatch operations, quality control is easier to maintain than with continuous flow systems, and this becomes very important when considering hazardous waste treatment.

Semibatch biological reactors (also called fill-and-draw, or sequencing batch reactors) may be composed of one or more reactors in series. The single reactor system appears to be well suited for many rural applications; the multiple reactor system, for industrial applications. One reactor can cycle through five discrete periods: fill, react, settle, draw, and idle. The idle period defines the time between the end of draw and the beginning of fill. An analysis of a multiple reactor system from a process control standpoint can be quite complex.

The mixed microbial populations used in the present study came from the Passaic Valley Sewerage Commissioners (PVSC) wastewater treatment plant in Newark, N.J.. This plant treats approximately 250 million gallons of waste per day, of which approximately 20 % by volume (and 55 % on a BOD basis) comes from industrial sources.

II. BACKGROUND

A. Literature Search:

An extensive amount of experimental and theoretical work on the biodegradation of phenol and other phenolic compounds using batch or continuous operation have been reported since 1950 [3-38]. Most of these publications have already been summarized by Desai [39], Colish [40], and Pak [41]. Hence, the literature search in this study concentrated on papers involving the use of fill-and-draw or sequencing batch reactors.

The computer data base containing Compendex, Oceanic Abstracts, Aquatic Science Abstracts, Georef, Fluidex, Aqualine, Water Resources Abstracts, EI Engineering Meetings, Waternet, and CA Search, was searched for the years 1970-1986. The following specific keywords were used: Fill-and-Draw Reactor, Semi-Batch Reactor, and Sequencing Batch Reactor. The search of Oceanic Abstracts, Aquatic Science Abstracts, Georef, and Waternet produced no result, but in Compendix, Fluidex, Aqualine, Water Resources Abstracts, EI Engineering Meeting, and CA search, 23 references were found, 5 of which had relevant subject matter. All these references were found using the keywords Fill-and-Draw and Sequencing Batch Reactor.

By using the affiliation index and the author index for the institutions and authors known to be active in this area, the abstracts of the Engineering Index for the years 1975-1985 were also searched. A total of 9 authors and 2 affiliations were used. At this point, the literature search was stopped, since most of the relevant articles had been found, and the list was becoming repetitious.

B. Literature Review:

Lewandowski and Abd-El-Bary [32] studied the biodegradation of phenol and 2-chlorophenol in shock-loaded 4-liter batch reactors, with an activated sludge from the Livingston, N.J. wastewater treatment plant. Phenol concentrations up to 500 ppm and 2-chlorophenol concentrations up to 50 ppm were investigated. At room temperature (25^{o}C), the degradation of phenol and 2-chlorophenol were found to follow a first order Grau model, with rate constants of 0.04/hr and 0.002/hr respectively. They also concluded that the addition of a co-substrate (sucrose) did not change the rate constant, but considerably increased the lag time.

Colish [40] used the same reactor and the same activated sludge to degrade phenol up to 500 ppm and 2-chlorophenol up to 40 ppm. For an assumed zero-order

mechanism, the rate constant for phenol (initially 100 ppm) ranged from 32 to 62 mg/l-hr. For 2-chlorophenol at a concentration of 20 ppm, the rate constant ranged from 3 to 5 mg/l-hr. Air stripping was determined to be an insignificant removal mechanism for the compounds studied. He also pointed out that the acclimation times decreased with repeated exposure to a particular concentration of phenol or 2-chlorophenol, and that the activated sludge bacteria first had to be acclimated to phenol before they could significantly degrade 2-chlorophenol (this also appeared to be the case in the present study).

In the study by Pak [41], the biological degradation of phenol (100 ppm), 2-chlorophenol (20 ppm), and 2,6-dichlorophenol (10 ppm) was studied at room temperature in aerated 5-liter batch reactors using mixed liquor from PVSC. He found the expression of zero-order kinetics to best represent the rates of substrate utilization for all three compounds (with first-order kinetics also showing a capability of fitting the experimental data). When the sludge was previously acclimated to 100 ppm phenol, he observed that the degradation rate for 2-chlorophenol increased by a factor of 30-40 %, and for 2,6-dichlorophenol by 30 % .

Caputi [42] has been studing the biodegradation of phenol (up to 500 ppm) and 2-chlorophenol (at 20 ppm) in a

continuous-flow stirred-tank reactor with solids recycle. He found some disadvantages in operating a continuous-flow reactor. These included: (1) the system was very sensitive to changes in waste strength or characteristics, pH, temperature, etc. ; (2) it was not easy to reach steady-state operation.

Many studies of the biodegradation of toxic wastes have been made using fill-and-draw or sequencing batch reactors. The following represents a survey of the existing literature.

Fill-and-draw technology is not new. In fact, it preceded the use of continuous-flow activated sludge technology. Ardern and Lockett [43] in 1914 were among the first to show the benefit of retaining substrate adapted organisms for efficient treatment. Working with 2 to 3 liter flasks containing raw wastewater from Manchester, England, they showed that the batch aeration period needed to achieve nitrification could be reduced from 5 weeks to 9 hours if the sludge that accumulated from each batch was retained in the flask after decanting the nitrified liquid. They coined the term "activated sludge" to describe the resultant biological mass. However, many difficulties were associated with operating these fill-and-draw systems, mostly resulting from the high degree of manual operator attention. Reliable process valving, timing, and switching

technology was not yet available to counter that deficiency. As a result of this, fill-and-draw systems were never applied to any great extent for municipal treatment after 1920. The birth and widespread use of continuous-flow systems resulted primarily from operational considerations and not from any process-related weaknesses of the fill-and-draw systems.

Times have changed. Development of new hardware devices, such as solenoid valves, pneumatic valves, level sensors, flow meters, automatic timers, and micro-processors or process controllers, has made it possible to revitalize semi-batch treatment technology.

The investigator primarily responsible for resuscitating fill-and-draw technology has been Robert Irvine at Notre Dame. Irvine and Davis [44] designed a waste treatment system which included three sequencing batch reactors and one continuous flow reactor. These reactors were designed to provide for equalization, treatment time, and sedimentation. Three fill-and-draw reactors in series were recommended for increased flexibility while maintaining simplicity of operation.

Irvine and Busch [45] described sequencing batch reactors and modern control strategies in an overview article. They concluded that SBR systems, because of their periodic nature, expand the spectrum of treatment

capabilities.

Simulation studies of sequencing batch reactors were conducted by Irvine and Richter [46,47,48,49]. They developed the design equations, along with experimental data in a 4 liter bench-scale reactor. A synthetic industrial waste with a soluble TOC concentration of approximately 500 mg/l was pumped into the reaction vessel. The results with fill times of two and four hours both showed relatively good agreement between measured and predicted values. They also concluded that reactors operated in the sequencing batch mode may provide stepwise equalization, quiescent sedimentation, and marked reductions in system volume, while insuring a control over effluent quality that cannot be achieved in conventional continuous-flow systems. In addition, the computer simulations showed how the design volume for a sequencing batch system differed as a function of the relative variability of the mass flow rate, even though the average mass flow rate was the same for all cases investigated.

Dennis and Irvine [50,51] studied the effect on sequencing batch reactors of fill time vs. react time. The experiments were conducted in 4 liter bench-scale plexiglass reactors. At all times during fill and react, the dissolved oxygen (DO) concentration was greater than 2.0 mg/l. The influent feed concentration, measured as 5-day biological

oxygen demand (BOD_5), was maintained at 400 mg/l. The corresponding filted total organic carbon concentration (FTOC) was 200 mg/l. The total cycle time was 8 hrs, in which 1 hr was used for settling and 1 hr for draw and idle. The three operational modes investigated were: 2-hr fill and 4-hr react; 4-hr fill and 2-hr react; and 5-hr fill and 1-hr react. They found that the average effluent soluble BOD_5 was 3 mg/l in all cases. However, there was a definite correlation between the settling velocity of the sludge and the fill-to-react ratio. The greatest velocity occured during the 2/4 mode while the lowest velocity occured during the 5/1 mode. Even though the MLSS concentration in the 4/2 experiment was approximately 600 mg/l higher than the 2/4 experiment, the trend toward a bulking, nonsettling sludge at the longer fill periods was evident. They also concluded that a properly designed semibatch reactor should achieve a higher effluent quality than a CSTR of similar size. Because of the ability to define a react period of suitable length, the wastewaters may be held in the treatment system until the desired effluent quality is achieved. This claim cannot be made for conventional continuous-flow systems.

The single tank batch system can be used for the treatment of wastewaters generated by rural municipalities and industries. Irvine, et al. [52] used wastewater collected at the University of Notre Dame, with a total BOD_5

of 220 mg/l, fed to a 5-liter bench-scale reactor. The initial volume was 2 liters and the final liquid volume was approximately 2.8 liters. The fill period was between 6 and 8 hours. A mechanical agitator was activated at the beginning of fill and deactivated 22-hour later, marking the end of react. The settle and draw periods were 1 hour each. Two sets of experiments were undertaken with different detention times (1.6 days and 3.5 days), and with different aeration strategies (full aeration during the fill period followed by 15-hr, 6-hr, or 3-hr aeration at the beginning of the react period). The results revealed that all the operating modes had the same effluent quality, with 95 % of BOD_5 removal and 5 mg/l of suspended solids (SS) in the discharge. These batch systems, with little design sophistication, will eliminate algae growth common to lagoon systems, provide for excellent BOD_5 and SS removal, and allow nitrification to proceed to completion.

Goronszy [53,54] described the application of continuously fed, intermittently operated systems to municipal wastes in Australia. His work provided little kinetic data, but described the advantages of such systems where flow and waste strength are highly variable or where trained operators and maintenance personnel are not available.

Bell and Hardcastle [55] also studied the treatment of

a high-strength industrial waste in a continuously fed, intermittently operated, activated sludge system. During the entire study, the system was operated on four cycles per day. In all cycles, the settling time was 45 minutes and the draw time was 15 minutes. The remaining 5 hours of each cycle were divided into aerobic and anoxic periods of various durations. For initial start-up the reactor was seeded with activated sludge from the Blue Plains Wastewater Treatment plant in Washington, D.C.. Over more than 30 months of study, various operating protocols were used. Organic removal was consistently high and nitrification and denitrification were essentially complete. Solids separation was good whenever dissolved oxygen levels were above 2.0 mg/l. They concluded that continuously fed, intermittently operated activated sludge system seem to be highly suitable for the treatment of high-strength industrial wastes containing organic solvents. Furthermore, the system was highly stable and extremely tolerant of changes in operating conditions, including shocks from power outages, mixer failure, and accidental overfeeds.

Zapf-Gilje and Mavinic [56] studied the characteristics of fill-and-draw reactors. Lysimeter generated leachate with BOD_5 of 13,640 mg/l (or TOC of 6,115 mg/l) and total metal ions of 2,086 mg/l (iron, calcium, magnesium etc.) was applied to a six liter, mixed liquor

reactor at a rate of 3.2 kg COD/m^3-day. This organic loading corresponded to a mean cell residence time of six days and a F/M ratio of 0.55 kg COD/kg MLVSS/day. The reactor was operated at a constant liquid temperature of 9°C with react periods of 12 hours and 24 hours. They found that treatment of the high strength leachate was controlled by zero-order metal oxidation and microbial growth. The mixed-liquor experienced a transition period following each leachate addition, but recovered within one-fourth of the react time. The organic removal and metal oxidations were almost complete after one-fourth of the react time. They also concluded that poor settling was attributed to: (1) nonfilamentous bulking and deflocculation caused by mixed-liquor upset following each feed cycle; and (2) hindered settling resulting from high MLSS concentrations.

Dagger and Grady [57] studied the factors affecting effluent quality from fill-and-draw activated sludge reactors. The microorganisms used in this study were obtained from a stock activated sludge culture obtained from the West Lafayette, Ind. wastewater treatment plant. Carbon was the growth-limiting nutrient and lactose served as the sole source of carbon and energy. The experimental reactors were round-bottom glass cylinders containing a liquid volume of 2.0 liters. The reactors were operated with a fill-and-draw cycle of 24 hours and a recycle ratio (volume of mixed

liquor remaining after withdrawal of supernatant/volume of feed added) of 1.0. Four influent substrate (lactose) concentrations were used: 600, 1600, 2600, and 3600 mg/l as COD. The most significant finding of this research is that the concentration of soluble COD in the effluent from a fill-and-draw activated sludge reactor is directly proportional to the concentration of biodegradable COD in the influent, when the mean cell residence time is maintained at a constant value. This finding has also been reported for continuous flow systems [58,59,60]. Therefore, if the influent concentration and its variability are of sufficient magnitude to cause significant changes in the concentration of soluble organic matter in the effluent, it will be necessary to adopt control strategies which use changes in the mean cell residence time to offset the effects of the changes in the influent concentration.

Filamentous growth can be easily controlled by varying the operating strategies during fill. Irvine [61] used an anaerobic period to minimize oxygen uptake rates during the fill portion of the cycle and found that both effluent quality and sludge compactability improved. Mixing was desirable during the anaerobic fill phase, because it enhanced partial conversion of the waste organics and released organically bound nitrogen.

Chiesa and Irvine [62] also reported the results of a

study in which sludge volume index (SVI) values were reduced from about 600 to 50 ml/g in a series of batch reactors subjected to varying, but controlled, operating strategies. Percent of aerated fill time was decreased successively from 100 % (for a SVI of about 600 mg/l) to 0 % (for a SVI of about 50 mg/l). They found that the best operating strategy in a SBR was to have a major portion of fill unmixed and unaerated, followed by mixing and aeration during the remaining 15 to 30 minutes of fill time.

Hoepker and Schroeder [63] studied the effect of loading rate on activated sludge effluent quality. Two types of systems were used in their experiments: batch (0 fill time) and semibatch (8-hour fill time). The batch system's organic carbon feed concentration ranged from 80 to 2560 g/m^3, while feed concentration in the semibatch reactors ranged from 160 to 640 g/m^3 . One-tenth of the reactor volume was wasted from each system each day. The results showed that: (1) the lower feed strength and lower feed rate had better effluent quality; (2) the semibatch systems were considerably more stable in terms of dispersed growth, even though a quantitative relationship with growth rate could not be established; and (3) the settling characteristics in batch systems improved with increased volumetric loading. They concluded that semibatch operations could be considered for most municipal plants,

either for overall operation or as a method of equalization.

Removal of nitrogenous impurities from wastewater can be accomplished through a variety of physicochemical and biological process alternatives. Biological removal offers an economic advantage and has therefore received the most attention. Ultimate conversion to gaseous nitrogen requires the coordinated coupling of two biochemical mechanisms -- nitrification and denitrification -- in oxidative and reductive reactions. The sequencing batch reactor (SBR) is basically a hybrid of the fill-and-draw configuration, which is capable of chronologically providing the required aerobic and anoxic conditions for nitrification and denitrification.

Alleman and Irvine [53,64,65,66] used a cylindrical plexiglass reactor (15 cm diam. x 50 cm length, with minimum and maximum volumes of 2.4 and 7.2 liters), and a synthetic, high strength influent waste stream. For nitrification experiments, the SBR consistently discharged a quality effluent with at least 98 % oxidation of both the organic carbon and nitrogen components. The operating conditions were: 2 hrs anoxic fill, 4 hrs aerobic react, 1 hr settle, 0.5 hr drain, and 1 hr idle. For denitrification studies, the SBR achieved a total nitrogen removal consistently above 92 %, without addition of supplemental carbon source. The react time in denitrification experiments was 6.33 hrs (consisting of 3 steps: 3 hrs

aeration, 3 hrs anoxic stir, and 0.33 hr aeration), instead of the 4 hrs single-step react in nitrification.

Biological phosphorus removal was first proposed in 1955 by Greenburgh et al. [67]. The flexibility of sequencing batch reactors is ideally suited to this goal, and this appears to be true even when operated as a non-nitrifying system. Ketchum and Liao [68] determined the feasibility of operating a chemical treatment, phosphorus reduction, tertiary-type clarifier in a fill-and-draw mode or as a sequencing batch reactor system. Although they did not make an actual operating cost analysis, significant cost savings were indicated by comparing chemical dosages needed to treat municipal wastewaters by conventional continuous flow methods with those needed when using the proposed sequencing batch reactor system. These savings in cost are a result not only of lower chemical costs but also of lower generated sludge volumes.

Manning and Irvine [69] also studied phosphorus removal using bench-scale fill-and-draw reactors. The 8-hour basic cycle used in the study typically included a 2-hour fill period, a 4-hour react period, and 2 hours for settling, draw, and idle. Different feeding and aeration strategies were tried during the fill phase. Results from this study showed that soluble phosphorus can be reduced from 13 g/m^3 to less than 0.5 g/m^3 in a fill-and-draw

reactor. This can be accomplished at an influent COD concentration of 330 g/m^3 and a total Kjeldahl nitrogen (TKN) of 44 g/m^3 . The SBR can also be designed to operate as a non-nitrifying system and still achieve biological phosphorus control. It appeared that an anoxic period with excess substrate allowed phosphorus-accumulating organisms to compete favorably. In addition, phosphorus release was hastened by the presence of soluble COD during anoxic periods.

Ketchum, et al. [70,71] studied two different modes of SBR operation. In the first case, all oxygen demands were satisfied, and in the second, oxygen was limited to that supplied by a constant rate aeration system operating at a rate less than would be needed to meet peak demands. Laboratory studies indicated an operating advantage where peak oxygen demands were not met. This mode of operation appeared to favor growth of nonfilamentous organisms and reduced the problems of bulking. Based on this second mode of operation, they also compared the estimated initial investment cost of the sequencing batch system with more conventional methods of treating wastewaters from relatively small communities. Four different design capacities were considered. For small rural communities (0.1 million gallons/day), costs appeared to be considerably less and effluent quality considerably higher than other methods of

treatment. Furthermore, operation of this facility should be less complex than operation of a conventional packaged plant. For small towns (1.0 mgd), nonaerated lagoons and conventional activated sludge systems appeared to offer no cost saving when compared to the cost of the sequencing batch system. The sequencing batch system will provide significantly higher quality effluents and result in about the same annual operating cost. For small and mid-size cities (5.0 and 10.0 mgd), although the lowest cost system in each of these these two cases is the aerated lagoon system, it does have the disadvantage of poor quality effluents and large land requirements. These two disadvantages, plus others, frequently prevent the use of lagoon systems.

Kamber and Whang [72] discussed the design of a sequencing batch activated sludge treatment plant for small flows of domestic sewage from two rural communities. They believed that in rural communities, batch reactors operating sequentially offer certain advantages over small continuous flow systems, including: (1) insensitivity to wide fluctuations in total flow; (2) net space-saving and simplification by elimination of separate components for clarification, sludge return, and flow equalization; (3) process adaptability without equipment modification; (4) improved process control and flexibility; and (5)

compatibility with a wide variety of effluent disposal options, including land application.

Arora, et al. [73] reported the results of a post-construction evaluation of sequencing batch reactors at several treatment plants in the U.S.. They visited eight plants and found there were no widely accepted or widely known standards for SBR design. Consequently, there was a wide range in design parameters, such as detention time, F/M ratio, and operating strategies at the facilities evaluated. Different water quality objectives (carbon, nitrogen, and phosphorus removals) were frequently achieved by appropriate changes in operating strategy. All the SBR plant operators reported that these facilities were easier to operate than the conventional continuous-flow systems. In their reports, Arora, et al. illustrated a step-by-step rational procedure that can be used to design a SBR system. They also developed different operating modes for different water quality objectives. Finally, they mentioned that all U.S. plants experienced some problems with their draw down decanter mechanisms. These problems, which stem from MLSS entering the decanter pipe during fill, react and settle periods, have been or are being corrected by returning the decanted effluent to the inlet end of the aeration basin during the first few minutes of draw down. However, the authors believed that improvements in decanter design were

needed, since this device is crucial to successful SBR operation.

Some investigators [47,70,73,74] reported the general advantages of using sequencing batch reactors. Among the salient points, the following are summarized:

* An SBR tank serves as an equalization basin during fill, and therefore can easily tolerate peak flows and shock loads of biochemical oxygen demand without degradation in effluent quality.

* Because effluent discharge is periodic, within limits, effluent may be held until it meets specified requirements.

* Chemical feed rates can be set to meet the exact requirements of the waste.

* Tanks can be easily taken on and off line as daily, seasonal and annual treatment requirements vary.

* Plant expansion would be simple.

* Mixed liquor suspended solids cannot be washed out by hydraulic surges, because they can be held in the tank as long as necessary. No return activated sludge pumping is required, because the mixed liquor is always in the reactor.

* Sedimentation can be guaranteed to take place in a totally quiescent environment. Short circuiting is nonexistent during the settle period

* Because the DO concentration is near zero during

anoxic fill, it provides for a greater oxygen driving gradient during the react period. This could achieve somewhat higher overall oxygen transfer efficiency with the same aeration equipment.

* The growth of filamentous microbes can be easily controlled by adjusting the operating strategy (feed rate and DO level) during fill.

* An SBR can be operated to achieve nitrification, denitrification, or phosphorus removal without chemical addition. Nitrification can be achieved by increasing the duration of react or by increasing the duration of the mixed/aerated portion of fill, while denitrification can be achieved by increasing the length of settle and draw (or both), so that near zero DO conditions are achieved during these periods. Phosphorus removal can be similarly accomplished by selecting a control strategy that lowers the DO level during fill (anaerobic rather than aerobic conditions) and allows for aeration during the react period. These variations in operating strategies are unique to the SBR systems and can be easily achieved by simple adjustments in the microprocessor settings.

An SBR demonstration for the treatment of municipal wastewaters was highly successful at Culver, Ind.. Irvine, et al. [75,76] reported the results of this performance. A two-tank SBR with equal volumes of 460 m^3 were used to treat

a domestic wastewater with BOD_5 ranging from 140 to 180 g/m^3. The daily average design flow was 1400 m^3/d. The results showed very efficient secondary treatment for the 18 months of SBR evaluation. Monthly average BOD_5 never exceeded 16 g/m^3, and SS never exceeded 15 g/m^3.

A further study of SBR operation at Culver, was also published by Irvine, et al. [77,78]. A wide range of operating potential was demonstrated by showing similar performance from two parallel SBRs: one with a sludge age of 9.5 days, a yield of 0.82 kg sludge waste per kilogram BOD_5 applied, and an organic loading of 0.42 kg BOD_5/kg MLVSS-d on an aeration time adjusted basis; and the other with a sludge age of 38 days, a yield of 0.56 kg/kg, and a corresponding loading of 0.16 kg BOD_5 /kg MLVSS-d. By comparision of these two system, two major conclusions were drawn. First, effluent quality from both SBRs was excellent. Slightly better quality was achieved from the reactor with lower loading. The more highly loaded reactor was more difficult to operate because of the tendency for the system to be underaerated for several days, a condition which then required one or two cycles of extra aeration. The periods of underaeration often resulted in higher effluent phosphorus concentrations while the periods of extra aeration seemed to produce higher concentrations of effluent suspended solids. These problems can be corrected

with microprocessor control of dissolved oxygen levels. Second, energy use in the more highly loaded system was about 30 % less than that for the system with lower loading, based on kilogram BOD_5 applied. This energy saving would be increased further if sludge was treated by anaerobic digestion and would be expected to be eliminated entirely if aerobic digestion was used. In addition, the extra sludge yield from the more highly loaded system may require bigger sludge handling equipment, assuming equal dewaterability.

The CECOS International Wastewater Treatment Plant in Niagara Falls, New York, was awarded a grant by New York State Energy Research and Development Authority to build a full scale SBR demonstration plant for the treatment of hazardous wastes (the combined waste feed had an average TOC concentration of 2618 mg/l). The following papers resulted from that study:

An initial study of SBR treatment of leachate was conducted by Irvine, et al. [79]. The results showed that the leachate was well treated in the small SBRs (working volume = 2 liters). About 90 % TOC reduction was achieved under a 24-hour cycle and 10-day hydraulic retention time schedule. Supplemental addition of a strain of bacteria isolated from the landfill site improved the treatment efficiency. Nitrogen and phosphate nutrients were not supplemented.

Herzbrun, et al. [80] reported the results of pilot plant studies. They operated four sequencing batch reactors at room temperature for a two month period. Retention times varied from 10 days down to 1.25 days. TOC degradation ranged from 55 to 81 %, and phenol degradation ranged from 96.8 to 99.2 % . Both ranges easily resulted in effluent concentrations that were within permit limits. Oxygen uptake rates and spiking studies indicated that the wastewater was readily biodegradable and that larger volumes of water could be handled in the full-scale reactor during peak periods. They also found that a one or two day power failure had no short or long term effect (such as elevated TOC or flotation of the sludge blanket) on system performance.

Ying, et al. [81] also undertook a comprehensive treatability study, utilizing three sets of SBRs : four 1-liter, four 12-liter, and three 500-liter. Up to 15 % variation in effluent TOC, COD and SS were observed for the replicated SBRs. Hyde Park leachate was well treated either alone or combined with other Niagara Plant wastewaters. The treatment performances were almost identical for the three sizes of SBRs when they were operated under the same conditions. Virtually the same performances were obtained for SBRs with several fill periods (2, 4, and 6 hours). Insufficient dissolved oxygen in the mixed liquor was the

major cause of low (<85 %) TOC removed. To treat 2000 mg TOC/l wastewater, about 150 mg DO/l-hr of oxygen transfer capability should be provided to the SBR operating at a MLSS of 10,000 mg/l. The oxygenation rate may be gradually reduced during the react period to satisfy the cell respiration rate of less than 4 mg DO/g MLVSS-hr. With at least 1 mg/l of DO during the react period, TOC and COD reductions were more than 90 % for the SBRs operated at a F/M as high as 0.2 mg TOC/mg MLSS-day. Cloudy effluents (SS > 250 mg/l), due to large populations of dispersed and/or filamentous bacteria, were caused by excessive organic loading, short react period, low DO, nutrient deficiency, and accumulation of toxic compounds. Effluent SS was less than 100 mg/l except when the feed TOC was higher than 3,000 mg/l. Finally, the SBR performance was nearly unchanged when the feeding was suspended on weekends or holidays.

In June 1984, CECOS started up a full-scale SBR demonstration facility at their treatment, storage, and disposal complex in Niagara Falls, New York [74,82]. A 500,000-gallon reactor was used to treat approximately 60,000 gal/day of wastewater that originated from landfill leachate, a ground-water remediation program, and receipt of wastewater from industrial generators. The major purpose of the SBR is to reduce the TOC load on a subsequent activated carbon system, and therefore reduce carbon regeneration

costs. According to CECOS, the SBR system performed successfully during its initial six months of operation. However, it was sensitive to rapid changes in influent quality. Thus, use of SBR in commercial treatment facilities appears to require a chemical equalization program to control the quality of wastewater entering the reactor. In this manner, upsets of the SBR bioorganisms may be minimized.

III. EXPERIMENTAL APPARATUS

A. FEEDING SYSTEM:

Nutrients plus substrate were mixed in a 20-gallon plastic carboy. For each feed cycle, 2 liters were transferred to a glass bottle via a microprocessor controlled solenoid valve. From the glass bottle, the feed was pumped to the fill-and-draw reactor with a peristaltic pump. Connections were made with 1/4" Tygon tubing.

B. REACTOR SET-UP:

All experiments were conducted in a 15 cm diameter, 6 liters capacity cylindrical vessel (constructed of Lucite), which was capped with a removable lid. An effluent port was placed at the one liter mark, and a solenoid valve was controlled to discharge the treated wastewater.

Stirring was supplied by an adjustable speed mixer with a 2-blade flat paddle impeller, which was positioned 3 cm from the bottom of the vessel.

Laboratory compressed air was supplied to the reactor by two 1/4" tygon tubes, after passing through an activated carbon and glass wool filter. The volume of air was

regulated by a needle valve rotameter and controlled by an air solenoid valve on each air line, so that the flow rate was zero (valves closed) or 60 cc/min x 2 (valves opened), respectively. To increase the efficiency of air/liquid contact, an aquarium diffuser stone was placed on the end of each air line at the bottom of the reactor.

The schematic diagram of this fill-and-draw reactor assembly is depicted in Figure #1.

C. CONTROLLER:

A microprocessor computer (Omron, Sysmac-PO sequence controller) controlled the system -- feed transfer solenoid valve, feed peristaltic pump, mixer, air solenoid valves, and decant solenoid valve. Any combination of fill, react, settle, and draw period times could easily be programmed into the computer.

IV. ANALYTICAL EQUIPMENT:

The following analytical equipment was used in the experimental procedures in this study :

1. Gas Chromatograph : Tracor model 565
   Operating Temperature
   Oven (a) phenol 160°C
   (b) o-chlorophenol 125°C for experiment 3, 4
   150°C for experiment 5-8
   Injection Port 300°C
   Detector 300°C
2. Automatic Injector : Varian, Aerograph
3. Automatic Sampler : Tracor, model 770
4. G. C. Column : Varian, 6' 1/8" SS
   10 % SP-2100 on 100/120
   Supelcoport
5. Electronic Integrator: Hewlett-Packard 3390A
6. DO & PH Meter : Orion Research,
   model 701A/Digital Ionalyzer
7. DO & PH Recorder : Kipp & Zonen, model BD401
8. DO Electrode : Orion Research, model 97-08
9. PH Electrode : Orion Research, model 91-04

V. EXPERIMENTAL PROCEDURES

A. SLUDGE PREPARATION:

Activated sludge was obtained from the Passaic Valley Sewerage Commissioners (PVSC), municipal wastewater treatment plant in Newark, New Jersey. The PVSC plant, located in a industrial area, treats approximately 250 million gallons per day of a waste that is about 30 % industrial and 70 % domestic. The plant uses oxygen (rather than air) in its activated sludge system.

The sample of mixed liquor was taken from the monitoring laboratory of the plant. A 10-liter bucket was used for transport of samples. As soon as the mixed liquor was brought to the laboratory, 3 liters were poured into a vessel and immediately provided with air. After aerating for a half hour, 2 liters of mixed liquor were poured into the fill-and-draw reactor. Another liter was taken to measure the fresh sludge MLSS concentration and sludge volume index.

B. FEED PREPARATION:

The influent solution contained carbon, nitrogen, and

phosphous as nutrients. Phenol or 2-chlorophenol was the sole carbon source, and ammonium carbonate / ammonium phosphate provided nitrogen, phosphorus, and buffer. The carbon : nitrogen : phosphorus mass ratio of the feed was approximately 100 : 14 : 3.

C. OPERATING STRATEGIES:

The batch operation of the reactor proceeded sequentially through 4 steps -- Fill, React, Settle, and Draw cycles. The common operating steps are described as follows:

In the fill phase, the first of four sequential operations, the influent pump to the reactor was started and the reactor contents were completely suspended by a variable speed mechanical agitator. The pumping rate was adjusted so that the total feed volume was exactly 2 liters during the fill period. There was no aeration. DO and pH were measured during all phases.

In the react phase, the influent pump and mixer were shut off, and the air solenoid valves were activated. Substrate samples were taken periodically. Upon completion of the timed react phase, the programmable controller turned the air valves off, and the reactor began a 20 minute settle phase.

During the settle phase, suspended solids settled to the bottom of the reactor, leaving a clear supernatant liquid. At end of this phase, the decant solenoid valve was activated by the progammable controller to remove the supernatant by gravity, leaving nearly all of the mixed liquor in the reactor. The draw phase lasted 10 minutes, which was enough to discharge two liters of supernatant.

A total of 8 experiments were conducted under various operating conditions at room temperature. Experiment I and experiment II were initially spiked to 100 ppm phenol, with a 2 hour feed phase using a 100 ppm phenol feed. The speed of mixing during the fill phase was 250 rpm for experiment I, and 25 rpm for all the other experiments. The degradation of 2-chlorophenol was examined in experiments IV and V. Finally, experiments III, VI, VII, and VIII examined the degradation of phenol followed by 2-chlorophenol.

A summary of experimental strategies is listed in Table #1.

VI. ANALYTICAL PROCEDURES

A. SUBSTRATE ANALYSIS:

The methods of analysis used for phenol and 2-chlorophenol were similar.

13 ml samples of the reactor fluid were taken during fill, react, or draw-down periods. The samples were centrifuged for 4 minutes at 2500 rpm, and 10 ml of supernatant were added to a sample vial containing 0.5 ml of 20,000 ppm copper sulfate which served as a biocide to stop the reaction (This had been verified previously [39,40].). The sample vials were sealed with tight fitting plastic caps and refrigerated. Before the samples were to be analyzed by gas chromatography, 0.5 ml of a 1000 ppm thymol solution were added to the vials as an internal standard.

The oven temperature of the GC depended on the substrate. It was 160^{o}C for phenol, and 125^{o}C (experiment III and experiment IV) to 150^{o}C (experiments V to VIII) for 2-chlorophenol. The reason for using two different oven temperatures with 2-chlorophenol is that the GC was repaired before the 5th experiment, and the retention characteristics changed. Each vial was injected 3 times, each time with 3-microliters of sample. The integrator automatically

calculated the concentration of each component in the sample. The accuracy of the GC analysis was approximately +/- 2.0 ppm.

B. MIXED LIQUOR SUSPENDED SOLIDS:

This is supposed to be an indication of the catalyst (i.e. biomass) concentration. Samples were taken from the reactor during the react and draw-down periods. Each time, the 10 ml fluid was withrawn and pipetted into a numbered, preweighed aluminum dish. The water was then evaporated in an oven at 95^{o}C for 24 hours, and the sample reweighed to determine the MLSS. This is a modification of a Standard Method [83].

C. DISSOLVED OXYGEN AND HYDROGEN ION CONCENTRATION:

The DO and pH of the reactor were continuously recorded on a two-pen plotter, using pH and DO electrodes. Occasionally, the electrodes were removed from the reactor, rinsed, recalibrated and placed back.

D. SLUDGE VOLUME INDEX (SVI):

The SVI is an indication of the efficiency of solids

separation in the system. The technique used was also a modification of a Standard Method [83,84]. For the base line inset, 500 ml of original sludge were mixed with 500 ml distilled water. Also, at the end of each experiment, 1 liter of mixed liquor were withdrawn from the reactor before the start of the settle period.

The 1 liter of mixed sample was placed rapidly into a 1-liter graduated glass cylinder, and the sludge volume determined after settling for 30 minutes.

To determine the SVI of the sample, the following calculation was needed:

$$SVI = \frac{\text{Settle Sludge Volume (ml/l) x 1000}}{\text{Mixed Liquor Suspended Solids (mg/l)}}$$

E. DISSOLVED OXYGEN UPTAKE RATE (DOUR):

200 ml of mixed liquor were withdrawn from the reactor at the beginning of the react period, then placed into a 250 ml BOD bottle. A DO electrode was inserted and the change (decrease) in dissolved oxygen level recorded with time. The slope of the curve is the dissolved oxygen uptake rate. Past studies in this laboratory [85,86] had indicated that the DOUR was a much better indicator of catalyst activity than MLSS.

VII. RESULTS AND DISCUSSION

A. BIODEGRADATION OF PHENOL:

Tables #2,3,4,7,8,9,11 and Figures #2,3,4,10,11 provide a summary of the phenol degradation results.

To compare the results of the fill-and-draw and batch modes, and as a check on reactor operation, experiments I and II were spiked to 100 ppm phenol before the first cycle. As can be seen from Figure #2, the average degradation rate in this case was 12 ppm/hr, which agrees with batch data previously obtained in this laboratory [39,40,41].

Table #2 and Figure #3 describe the results of experiment I. The system reached steady-state by the third cycle. The average degradation rate at steady-state (for a feed concentration of 100 ppm) was 55 ppm/hr (with a range of 51 to 58 ppm/hr). In subsequent experiments, the fourth cycle was chosen for data collection , as indicative of steady-state. In Table #3 and Figure #3, the fourth cycle in experiment II confirmed this selection, in which the degradation rate was 58 ppm/hr.

As the influent phenol concentration was raised to 200-300 ppm, the average degradation rate at steady state increased to 75 ppm/hr (see Tables #4 and 9; and Figures #4

and 10).

By the fourth cycle, the organisms were acclimated to phenol, and a 2-hr react phase was sufficient to lower the concentration below the GC detection limit (1 ppm) (Table #9, Figure #10). However, in the earlier experiments (I to IV), a 5.5 hour react time had been arbitrarily preset. Therefore, for approximately 4 hours (including draw-down time), the organisms were without a carbon source. This probably resulted in endogenous respiration, so that the next cycle needed some lag time to recover microbial activity. This would explain the increased degradation rate (to 96 ppm/hr) when the react time was reduced to 2 hours (Figure #11).

In commercial fill-and-draw operations, the aerated reaction time can be adjusted until the effluent meets specified requirements.

In each cycle of the same experiment, a comparison of the feed concentration with the concentration at the end of the fill period shows that there is almost no phenol degradation occurring during the fill phase. Similarly, a comparison of the effluent concentration on draw-down with the concentration at the end of the react period shows no significant degradation occurring during the settle and draw phases. These two observations indicate that the phenol is not degraded under anoxic conditions. Also, it is clear

that changes in feed time (2 hrs or 0.5 hr) or mixing speed (250 rpm or 25 ppm) during the fill phase made no difference in the final results.

B. BIODEGRADATION OF 2-CHLOROPHENOL:

Tables #4,5,6,7,8,9,11 and Figures #5,6,7,8,9,12 provide a summary of 2-chlorophenol degradation results.

The degradation of 2-chlorophenol, using an unacclimated sludge was studied in experiments IV and V. As can be seen from Tables #5,6 and Figures #6,7, the average degradation rate for a 20 ppm feed concentration, and 8 hour cycle time (2-hr Fill and 5.5-hr React) was 0.19 ppm/hr; and that for a 30 ppm feed concentration, and 12 hour cycle time (0.5-hr Fill and 11-hr React) was 0.10 ppm/hr.

The degradation of 2-chlorophenol after phenol acclimation was also investigated. It was found that raising the influent phenol concentration, and lengthening the acclimation time in previous cycles, promote the degradation rate in the following 2-chlorophenol runs. For a cycle with 2-hr Fill, 5.5-hr React, experiment III showed that the average degradation rate after the third 2-chlorophenol cycle (steady-state) was 0.33 ppm/hr, (see Table #4 and Figure #5).

Experiments VI to VIII were all under the condition of

0.5-hr Fill and 11-hr React for 2-chlorophenol runs, with microbes previously acclimated by a 3-hour phenol cycle (0.5-hr Fill and 2-hr React). The steady-state degradation rate of 2-chlorophenol varied from 0.51 ppm/hr (after acclimation to 20 ppm phenol), to 1.4 ppm/hr (after acclimation to 300 ppm phenol). These results are shown in Table #7 (Figure #8) and Table #8 (Figure #9), respectively. Furthermore, the results shown in Table #9 and Figure #12 indicated that a well-acclimated sludge could increase the degradation rate of 2-chlorophenol to 3.5 ppm/hr.

To explain the results above, it is assumed that the necessary enzymes for phenol digestion are parts of the enzymes required to degrade the 2-chlorophenol.

In Table #8, the microbes did not degrade the phenol rapidly enough in the first few cycles, so that upon feeding 2-chlorophenol, two substrates coexisted in the system.

C. DISSOLVED OXYGEN CONCENTRATION:

During the react phase, if the air supply rate was a constant equal to 120 cc/min, it was found that the following three types of dissolved oxygen (DO) concentration curves with different substrate and operating strategies were obtained.

1. In Figure #4 and #10, initially, the DO concentration

increased since the DO uptake rate was lower than the DO supply rate; as the uptake rate increased (indicating acclimation), the DO concentration leveled off and then started to drop; until the carbon source (phenol) was exhausted, at which point respiration was much reduced and the DO level rose once more.

2. In Figure #11, with the same phenol inflow but a shorter react time, the DO concentration stayed low upon starting the react phase. The shorter react time meant that the phenol from the previous cycle had just been degraded and the organisms were still active.

3. In Figure #5,6,8,9, and 12, the DO concentration directly rose to a solubility maximum during the first half-hour of the react phase. Perhaps because of the low concentration of substrate (20 ppm 2-chlorophenol), the microbial respiration rate was far exceeded by the oxygen supply rate.

D. OXYGEN UPTAKE RATES:

The oxygen uptake rate (OUR) can be considered as an important parameter indicating the activity of microbes. In this study, the OUR was measured only at initiation of react phase during a steady-state cycle. The results are listed in Table #10.

Since phenol is more easily biodegraded, the corresponding OUR's are higher.

E. HYDROGEN-ION CONCENTRATION:

In 2-chlorophenol degradation, the pH seemed to be related to the dissolved oxygen content, and pH rose as DO concentration increased (see Figure #13). However in phenol degradation, pH decreased as the reaction proceeded (see Figure #14). For all experiments, the pH range was 6.7 to 7.2 (see Tables #1 to 9).

F. SETTLING CHARACTERISTICS:

There are two measurements which indicate the settling characteristics of the biomass: the Sludge Volume Index (SVI) and Effluent Mixed Liquor Suspended Solids (EMLSS), as shown in Table #2 and 9. In general, it was found that the SVI was low enough that solids separation was rapid and complete. However, the results of EMLSS measurements showed that the settleability greatly improved from the initial cycle to steady-state. In the first cycle, the EMLSS reached as high as 450-750 mg/l.

VIII. CONCLUSIONS

1. The flexibility of fill-and-draw reactors was clearly demonstrated in this study. Any combination of Fill, React, Settle, and Draw-Down times can be accomodated, each under aerated or anoxic conditions, by using a programmable controller.
2. Phenol was degraded at rates up to 96 ppm/hr, for feed concentrations up to 300 ppm.
3. 2-Chlorophenol was degraded at 0.10 to 0.19 ppm/hr for a 20 ppm feed, and up to 3.5 ppm/hr when the organisms were pre-acclimated to phenol.
4. Measurement of dissolved oxygen concentration, and DO uptake rate, offers a good way of estimating microbial activity, and also an indication of when the substrate is depleted.

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Table #1 Experimental Strategies

Exp.	Cycle	Feeding Substrate	Conc. (ppm)	Time Sharing Fill* (hrs)	React** (hrs)	Settle (mins)	Draw (mins)
I	All	Phenol ***	100	2	5.5	20	10
II	All	Phenol ***	100	2	5.5	20	10
III	1- 5	Phenol	200	2	5.5	20	10
	6-10	2-C-Phenol	20	2	5.5	20	10
IV	All	2-C-Phenol	20	2	5.5	20	10
V	All	2-C-Phenol	30	0.5	11	20	10
VI	1- 4	Phenol	20	0.5	2	20	10
	5- 9	2-C-Phenol	30	0.5	11	20	10
VII	1- 4	Phenol	300	0.5	2	20	10
	5-12	2-C-Phenol	30	0.5	11	20	10
VIII	1- 5	Phenol	300	2	5.5	20	10
	6- 9	Phenol	300	0.5	2	20	10
	10-13	2-C-Phenol	30	0.5	11	20	10

* Anoxic mixing during fill phase.
** Aeration but no mixing during react phase.
*** Spiked to 100 ppm phenol at initiation of first cycle.

Note 1: All experiment were runing at room temperature which was $20^{o}C$ - $28^{o}C$.
2: Speed of mixing during fill phase was 250 rpm in first experiment and 25 rpm for the others.

Table #2 Results of Experiment I
(Inflow: 100 ppm phenol; Spike to 100 ppm phenol at initial)

Cycle	Date	Time	State Sample Taken From	MLSS (mg/l)	PH	DO (mg/l)	Substrate Conc. (ppm)
1	6/14	11:45	Inflow				109.503
		12:39	After Feed	3275		0.78	104.747
		13:09	React 0.5 hr				105.320
		13:39	1		6.89	3.58	101.685
		14:09	1.5 hrs				96.742
		14:39	2			6.29	89.709
		15:09	2.5				84.665
		15:39	3				79.391
		16:09	3.5				74.550
		16:39	4				71.101
		17:09	4.5				58.116
		17:39	5				47.026
		18:09	After React	3225			37.086
		18:39	Effluent				38.229
2		20:39	After Feed				70.228
	6/15	2:09	After React				0.0
		2:39	Effluent				0.
3		4:39	After Feed				52.375
		4:49	React 10 mins				44.366
		4.59	20				34.197
		5:09	30				23.812
		5:39	1 hr				0.0
		6:39	2 hrs				0.0
		10:09	After React				0.0
		10:39	Effluent				0.0
4		12:39	After Feed				50.068
		12:49	React 10 mins				42.737
		12:59	20		6.84	4.78	34.751
		13:09	30				24.537
		13:39	1 hr				0.0
		14:39	2 hrs				0.0
		18:09	After React	3025	7.08	7.18	0.0
		18:39	Effluent				0.0

Table #2 Continued

Cycle	Date	Time	State Sample Taken From	MLSS (mg/l)	PH	DO (mg/l)	Substrate conc. (ppm)
5		20:39	After Feed		6.78	0.81	52.113
		21:39	React 1 hr				0.0
		22:39	React 2 hrs			7.15	0.0
	6/16	2:09	After React		7.10	7.23	0.0
		2:39	Effluent				0.0
6		4:39	After Feed				51.309
		10:09	After React				0.340
		10:39	Effluent				0.0
7		12:39	After Feed				45.148
		18:09	After React	2650			0.0
		18:39	Effluent				0.0
8		20:39	After Feed				47.481
	6/17	2:09	After React				0.0
		2:39	Effluent	300			0.0
9		4:39	After Feed		6.82	0.83	53.899
		4:49	React 10 mins				46.937
		4:59	20				37.755
		5:09	30				25.319
		5:39	1 hr				0.0
		6:39	2 hrs				0.0
		8:39	4				0.0
		10:09	After React	2475	7.13	7.38	0.0
		10:39	Effluent				0.0

Note: Speed of mixing during feed period was 250 rpm.

Table #3 Results of Experiment II
(Inflow: 100 ppm phenol; Spike to 100 ppm phenol at initial)

Cycle	Date	Time	State Sample Taken From	MLSS (mg/l)	PH	DO (mg/l)	Substrate Conc. (ppm)
1	6/28	15:12	After Feed	2675	6.87	0.15	116.100
		20:42	After React	2600	7.35	5.61	69.630
		21:12	Effluent	750			62.443
2		23:12	After Feed			0.10	89.480
	6/29	4:42	After React	2300		7.50	
		5:12	Effluent	500			0.0
3		7:12	After Feed			0.12	49.298
		12:42	After React	2050	7.47	8.16	
		13:12	Effluent	450			0.0
4		14:50	Inflow				102.675
		15:12	After Feed		6.86	0.09	52.431
		15:22	React 10 mins			3.10	44.542
		15:32	20			2:71	34.096
		15:42	30			2.20	23.854
		15:52	40			1.69	14.395
		16:02	50			1.25	
		16:12	1 hr		7.21	5.53	0.0
		16.42	1.5 hrs			7.88	0.0
		17:12	2		7.36	7.92	0.0
		17:42	2.5			8.01	0.0
		18:12	3		7.36	7.98	0.0
		18:42	3.5			8.03	0.0
		19:12	4		7.37	8.02	0.0
		19:42	4.5			7.99	0.0
		20:12	5			8.01	0.0
		20:42	After React	2100	7.37	8.03	0.0

Note 1: Speed of mixing changed to 25 rpm since experiment II.
2: Sludge volume index at initial and final was 48.6 , 37.3 respectively.

Table #4 Results of Experiment III
(Inflow: cycle 1-5 200 ppm phenol, cycle 6-10 20 ppm 2-chlorophenol)

Cycle	Date	Time	State Sample Taken From	MLSS (mg/l)	PH	DO (mg/l)	Substrate Conc. (ppm)
1	7/18	14:38	After Feed	2700			
		20:38	Effluent	650			
3	7/19	6:38	After Feed		6.91	0.08	127.720
		7:08	React 0.5 hr		7.07	5.02	110.590
		7:38	1		6.98	4.06	82.650
		8:08	1.5 hrs		6.86	2.80	53.046
		12:08	After React		7.12	6.70	0.183
4		14:07	Inflow				217.725
		14:38	After Feed		7.19	0.10	102.650
		14:48	React 10 mins		7.11	4.01	95.600
		14:58	20		7.05	4.00	86.590
		15:08	30		7.00	3.42	75.143
		15:18	40		6.94	2.61	64.078
		15:28	50		6.89	1.82	49.572
		15:38	1 hr		6.82	0.78	35.908
		15:48	70 mins		6.80	0.40	21.065
		15:58	80		6.79	0.26	0.598
		16:08	90		6.90	4.21	0.0
		16:18	100		7.04	6.21	0.0
		16:28	110		7.18	7.02	0.0
		16:38	2 hrs		7.28	7.39	0.0
		17:08	2.5		7.46	7.75	0.0
		17:38	3		7.51	7.92	0.0
		18:08	3.5		7.60	7.99	0.0
		18:38	4		7.61	8.00	0.0
		19:08	4.5		7.60	8.01	0.0
		20:08	After React	1550	7.60	8.00	0.0
		20:38	Effluent	400			0.0
5		20:43	Feed 5 mins		7.06*	0.20**	11.980
		20:48	10		7.06	0.10	18.340
		20:58	20		7.07	0.10	30.936
		21:08	30		7.06	0.10	39.298
		21:38	1 hr		7.08	0.10	72.337

Table #4 Continued

Cycle	Date	Time	State Sample Taken From	MLSS (mg/l)	PH	DO (mg/l)	Substrate Conc. (ppm)
5	7/19	22:08	Feed 1.5 hrs		7.07	0.10	88.831
		22:38	After Feed		7.09	0.10	100.435
	7/20	4:08	After React	1350			
Start to feeding 2-chlorophenol since cycle 6. ***							
8		22:38	After Feed		6.92	0.03	17.310
		23:08	React 0.5 hr		7.39	6.58	16.993
		23:38	1		7.59	6.69	16.491
	7/21	0:08	1.5 hrs		7.55	6.71	16.122
		4:08	After React		7.57	6.71	14.999
9		6:32	Inflow				20.986
		6.38	After Feed		7.01	0.04	16.252
		7:08	React 0.5 hr		7.49	6.93	16.191
		7:38	1		7.58	6.98	15.523
		8.08	1.5 hrs		7.56	7.00	15.579
		8:38	2		7.56	7.00	15.267
		9:08	2.5				15.269
		9:38	3				15.137
		10:08	3.5				15.101
		11:08	4.5				14.857
		12:08	After React	1400	7.56	6.99	14.819
		12:38	Effluent	450			
10		13:38	Feed 1 hr				15.310
		14:38	After Feed				16.390
		20:08	After React	1400			14.538

* PH dropped down from 7.51 to 7.09 at initial 4 minutes.
** DO linearly dropped down from 6.60 to 0.20 at initial 4 minutes.
*** No data recorded during cycle 6, 7.

Note: Sludge volume index at initial and final was 50.0 , 56.4 respectively.

Table #5 Results of Experiment IV
(Inflow: 20 ppm 2-chlorophenol; No phenol acclimated)

Cycle	Date	Time	State Sample Taken From	MLSS (mg/l)	PH	DO (mg/l)	Substrate Conc. (ppm)
1	7/30	17:00	After Feed	2475	7.09	0.78	9.683
		22:30	After React				9.501
		23:00	Effluent				9.496
2	7/20	1:00	After Feed		7.15	0.22	
		6:30	After React		7.67	7.45	
3		9:00	After Feed				16.821
		14:30	After React				16.086
		15:00	Effluent				16.040
4		16:30	Inflow				19.380
		17:00	After Feed		6.99	0.16	18.061
		17:30	React 0.5 hr		7.37	7.62	18.045
		18:00	1		7.58	7.70	18.083
		18:30	1.5 hrs		7.58	7.69	17.965
		19:00	2		7.60	7.65	17.909
		19:30	2.5		7.61	7.65	17.622
		20:00	3		7.63	7.64	17.627
		20:30	3.5		7.62	7.60	17.429
		21:00	4				17.562
		21:30	4.5				17.283
		22:00	5				17.224
		22:30	After React	1900	7.64	7.60	17.055
		23:00	Effluent	300			16.814
5		23/30	Feed 0.5 hr				17.822
	8/1	0:00	1				18.016
		0:30	1.5 hrs				18.118
		1:00	After feed				18.320
		6:30	After React	1650			

Note: Sludge volume index at initial and final was 48.5 , 61.2 respectively.

Table #6 Results of Experiment V
(Inflow: 30 ppm 2-chlorophenol; No phenol acclimated)

Cycle	Date	Time	State Sample Taken From	MLSS (mg/l)	PH	DO (mg/l)	Substrate Conc. (ppm)
1	8/19	12:52	After Feed	2600			13.414
	8/20	0:22	Effluent				11.840
2		0:52	After Feed				19.470
		11:52	After React	1800			
		12:22	Effluent				18.184
3		12:52	After Feed				22.032
	8/21	0:22	Effluent				20.496
4		0:30	Inflow				30.190
		0:52	After Feed		7.45	7.51	23.425
		1:52	React 1 hr		7.63	7.85	23.364
		2.52	2 hrs		7.67	7.83	23.677
		3:52	3				22.786
		4:52	4				23.284
		6:52	6				22.946
		7:52	7				22.669
		9:52	9				22.518
		10:52	10				22.245
		11:52	After React	2000	7.65	7.83	22.292
		12:22	Effluent	150			22.679
5		12:52	After Feed				24.767
	8/22	0:22	Effluent				24.488
6		0:52	After feed				24.912
		11:52	After React	1950			
		12:22	Effluent				22.913
7		12:52	After Feed				25.336
	8/23	0:22	Effluent				25.410

Table #6 Continued

Cycle	Date	Time	State Sample Taken From	MLSS (mg/l)	PH	DO (mg/l)	Substrate Conc. (ppm)
8	8/23	0:52	After Feed		7.51	6.70	25.624
		1:52	React 1 hr		7.72	8.40	25.608
		2:52	2 hrs		7.72	8.40	24.922
		3:52	3				25.256
		4:52	4				25.597
		5:52	5				25.523
		6:52	React 6				25.326
		8:52	8				25.369
		9:52	9				25.256
		10:52	10				25.220
		11:52	After React	1700	7.71	8.38	25.162
		12:22	Effluent	250			25.751
9		12:52	After Feed				26.069
	8/24	0:22	Effluent				26.003
10		0:52	After Feed *				26.593
		11:52	After React	1600			
		12:22	Effluent				25.809
11		12:52	After Feed				27.397
	8/25	0:22	Effluent				27.072
12		0:30	Inflow				30.244
		0:52	After Feed		7.47	6.34	28.132
		1:52	React 1 hr		7.70	8.20	27.848
		2:52	2 hrs		7.70	8.19	27.297
		3:52	3				27.644
		4:52	4				27.094
		5:52	5				26.910
		6:52	6				27.488
		7:52	7				27.296
		9:52	9				26.859
		10:52	10				26.441
		11:52	After React	1400	7.68	8.17	26.208
		12:22	Effluent	100			25.279

Table #6 Continued

Cycle	Date	Time	State Sample Taken From	MLSS (mg/l)	PH	DO (mg/l)	Substrate Conc. (ppm)
18	8/28	0:52	After Feed		7.45	6.28	31.135
		11:52	After React	1100	7.65	8.09	
		12:22	Effluent				30.756

* Influent conc. was changed from 30.190 to 30.244 since cycle 10.

Note 1: No data recored during cycle 13 - 17.
2: Sludge volume index at initial and final was 65.4 , 67.3 respectively.

Table #7 Results of Experiment VI
(Inflow: cycle 1-4 20 ppm phenol, cycle 5-9 30 ppm 2-chlorophenol)

Cycle	Date	Time	State Sample Taken From	MLSS (mg/l)	PH	DO (mg/l)	Substrate Conc. (ppm)
1	9/6	10:40	After Feed	3500			
2		13:40	After Feed				19.843
		16:10	Effluent				3.657
3		16:40	After Feed		6.70	0.10	15.964
		18:40	After React		7.00	5.80	
		19:10	Effluent				4.299
4		19:30	Inflow				17.899
		19:40	After Feed		6.50	0.12	7.306
		19:55	React 15 mins		6.79	3.98	0.672
		20:10	30		6.90	5.23	0.0
		20:25	45		7.02	6.10	0.0
		20:40	60		7.08	6.15	0.0
		21:10	90		7.13	6.36	0.0
		21.40	After React	3000	7.13	6.35	0.0

Start to feeding 2-chlorophenol since cycle 5.

5		22:40	After Feed		6.75	0.20	11.868
	9/7	9:40	After React		7.02	6.20	
		10:10	Effluent				3.158
6		10:40	After Feed		6.89	1.80	14.105
		21:40	After React		7.24	7.72	
		22:10	Effluent	300			6.034
7		22:40	After Feed		6.80	1.15	15.771
	9/8	9:40	After React		7.25	6.96	
		10:10	Effluent				10.842

Table #7 Continued

Cycle	Date	Time	State Sample Taken From	MLSS (mg/l)	PH	DO (mg/l)	Substrate Conc. (ppm)
8	9/8	10:20	Inflow				29.632
		10:40	After Feed		7.09	2.20	21.061
		11:40	React 1 hr		7.54	7.15	20.581
		12:40	2 hrs		7.55	7.17	19.253
		13:40	3		7.53	7.15	18.927
		15:40	5				17.360
		16:40	6				16.895
		17:40	7				16.728
		19:40	9				16.257
		21:40	After React	2100	7.55	7.16	15.593
		22:10	Effluent				15.253
9		22:40	After Feed				23.142
	9/9	10:10	Effluent				18.240

Note: Sludge volume index at initial and final was 45.7 , 73.8 respectively.

Table #8 Results of Experiment VII
(Inflow: cycle 1-4 300 ppm phenol, cycle 5-12 30 ppm 2-chlorophenol)

Cycle	Date	Time	State Sample Taken From	MLSS (mg/l)	PH	DO (mg/l)	Substrate Conc. (ppm)
1	9/13	11:30	After Feed	3225			129.360
		14:00	Effluent				128.323
2		14:30	After Feed				197.923
		17:00	Effluent				196.411
3		17:30	After Feed				232.915
		20:00	Effluent				230.604
4		20:25	Inflow				274.731
		20:30	After Feed		7.21	4.00	250.009
		21:30	React 1 hr		7.50	8.97	248.885
		22:30	After React	2500	7.48	9.05	247.383
		23:00	Effluent				245.135

Start to feeding 2-chlorophenol since cycle 5.

5		23:30	After Feed		7.00	3.35	p 126.020*
							o 16.300
	9/14	10:30	After React		7.29	8.65	
		11:00	Effluent				p 78.109*
							o 13.949
6		11:30	After Feed		6.69	1.40	p 20.738*
							o 23.275
		22:30	After React	2250	7.02	8.32	
		23:00	Effluent	100			p 0.0
							o 9.459

Table #8 Continued

Cycle	Date	Time	State Sample Taken From	MLSS (mg/l)	PH	DO (mg/l)	Substrate Conc. (ppm)
7	9/14	23:30	After Feed		6.75	4.03	17.170
	9/15	10:30	After React		7.21	8.89	
		11:00	Effluent				4.969
8		11:15	Inflow				32.601
		11:30	After Feed		6.70	4.05	16.117
		12:30	React 1 hr		7.18	8.99	14.566
		13:30	2 hrs		7.20	8.99	13.706
		15:30	4				10.865
		17:30	6				8.276
		19:30	8				5.414
		21:30	10				2.578
		22:30	After Feed	2350	7.19	8.98	1.038
		23:00	Effluent	150			1.064
9		23:30	After Feed**		6.78	2.55	10.989
	9/16	10:30	After React		7.20	8.40	0.0
		11:00	Effluent				0.0
10		11:30	After Feed			3.05	12.232
		22:30	After React	2100		8.49	0.0
		23:00	Effluent				0.0
11		23:30	After Feed				9.989
	9/17	11:00	Effluent				0.0

Table #8 Continued

Cycle	Date	Time	State Sample Taken From	MLSS (mg/l)	PH	DO (mg/l)	Substrate Conc. (ppm)
12	9/17	11:15	Inflow				17.113
		11:30	After Feed		6.61	2.53	7.585
		12:30	React 1 hr		6.99	8.49	6.193
		13:30	2 hrs		6.98	8.47	4.913
		14:30	3				3.462
		16:30	5				0.494
		17:30	6				0.0
		19:30	8				0.0
		21:30	10				0.0
		22:30	After React	2050	7.00	8.49	0.0
		23:00	Effluent	150			0.0

* Both phenol and 2-chlorophenol existed.
** Influent conc. was changed from 32.601 to 17.113 since cycle 9.

Note: Sludge volume index at initial and final was 48.4 , 69.3 respectively.

Table #9 Results of Experiment VIII
(Inflow: cycle 1-9 300 ppm phenol, cycle 10-13 30 ppm 2-chlorophenol)

Cycle	Date	Time	State Sample Taken From	MLSS (mg/l)	PH	DO (mg/l)	Substrate Conc. (ppm)
1	10/28	12:02	After Feed	2700	7.19	0.25	147.600
		17:32	After React		7.56	6.48	
		18:02	Effluent	450			101.085
2		20:02	After Feed		7.16	0.18	195.610
	10/29	1:32	After React		7.30	6.41	
		2:02	Effluent				102.267
3		4:02	After Feed		7.00	0.18	189.240
		9:32	After React		7.12	6.60	
		10:02	Effluent	200			8.466
4		11:20	Inflow				299.840
		12:02	After Feed		6.81	0.18	147.180
		12:12	React 10 mins		6.90	3.21	140.250
		12:22	20		6.88	3.61	129.550
		12:32	30		6.86	3.52	120.740
		12:42	40		6.82	3.25	108.625
		12:52	50		6.80	2.83	98.698
		13:02	1 hr		6.77	2.25	84.674
		13:12	70 mins		6.71	1.38	72.600
		13:22	80		6.69	0.81	58.402
		13:32	90		6.65	0.62	41.713
		13:42	100		6.63	0.45	25.203
		13:52	110		6.62	0.31	11.047
		14:02	2 hrs		6.71	2.67	0.0
		14:12	130 mins		6.78	4.75	0.0
		14:22	140		6.86	5.39	0.0
		14:32	2.5 hrs		6.88	5.51	0.0
		15:02	3		6.91	5.92	0.0
		15:32	3.5		7.09	6.95	0.0
		16:32	4.5		7.12	7.14	0.0
		17:32	After React	2200	7.12	7.15	0.0
		18:02	Effluent	200			0.0

Table #9 Continued

Cycle	Date	Time	State Sample Taken From	MLSS (mg/l)	PH	DO (mg/l)	Substrate Conc. (ppm)
5	10/29	18:32	Feed 0.5 hr		6.80	0.17 *	59.020
		19:02	1		6.80	0.17	92.318
		19:32	1.5 hrs		6.80	0.17	120.610
		20:02	After Feed		6.80	0.17	142.860
	10/30	1:32	After React	2550	7.04	6.85	0.0
		2:02	Effluent	200			0.0
6		2:32	After Feed		6.78	0.11	129.890
		4:32	After React	2300	6.77	5.64	
		5:02	Effluent				0.0
7		5:32	After Feed		6.64	0.10	128.350
		7:32	After React	2550	6.78	5.86	
		8:02	Effluent				0.0
8		8:32	After Feed		6.62	0.10	121.050
		10:32	After React	2550	6.71	5.64	
		11:02	Effluent				0.0
9		11:32	After Feed		6.60	0.10	113.180
		11:42	React 10 mins		6.54	0.20	95.076
		11:52	20		6.48	0.18	82.992
		12:02	30		6.42	0.15	69.411
		12:12	40		6.38	0.17	51.037
		12:22	50		6.38	0.16	33.517
		12:32	1 hr		6.40	0.12	17.895
		12:42	70 mins		6.41	0.10	0.153
		12:52	80		6.51	3.18	0.0
		13:12	100		6.68	4.85	0.0
		13:32	After React	2500	6.85	5.50	0.0
		14:02	Effluent	150			0.0

Start to feeding 2-chlorophenol since cycle 10.

Table #9 Continued

Cycle	Date	Time	State sample Taken From	MLSS (mg/l)	PH	DO (mg/l)	Substrate Conc. (ppm)
10	10/30	14:32	After Feed		6.55	0.09	12.317
	10/31	1:32	After React	2300	6.95	6.68	
		2:02	Effluent	100			0.030
11		2:32	After Feed		6.54	0.08	11.629
		13:32	After React		6.98	6.70	
		14:02	Effluent	50			0.033
12		14:32	After Feed		6.60	0.08	11.258
	11/01	1:32	After React	2100	7.05	6.90	
		2:02	Effluent	100			0.026
13		2:15	Inflow				37.976
		2:32	After Feed		6.72	0.08	11.589
		3:32	React 1 hr		7.16	6.75	6.459
		4:32	2 hrs		7.20	6.83	3.259
		5:32	3		7.22	6.88	1.008
		6:32	4		7.25	6.83	0.0
		7:32	5		7.25	6.82	0.0
		8:32	6		7.26	6.83	0.0
		9:32	7				0.0
		10:32	8				0.0
		11:32	9				0.0
		12:32	10				0.0
		13:32	After React	2050	7.26	6.80	0.0
		14:02	Effluent				0.0

* DO linearly dropped down from 6.23 to 0.17 at initial 4 minutes.

Note: Sludge volume index at initial and final was 66.3 , 83.4 .

Table #10 **Results of Oxygen Uptake Rates**

Substrate	Experiment	Cycle	OUR (mg DO/g-MLSS-hr)
Phenol	III	5	41.6
	VIII	5	43.4
2-Chlorophenol	III	10	1.1
	IV	5	1.1
	VII	13	1.1

Table #11 Summary of Zero-order Kinetic Constant

Zero order model : $S_o - S = K\ t$

where

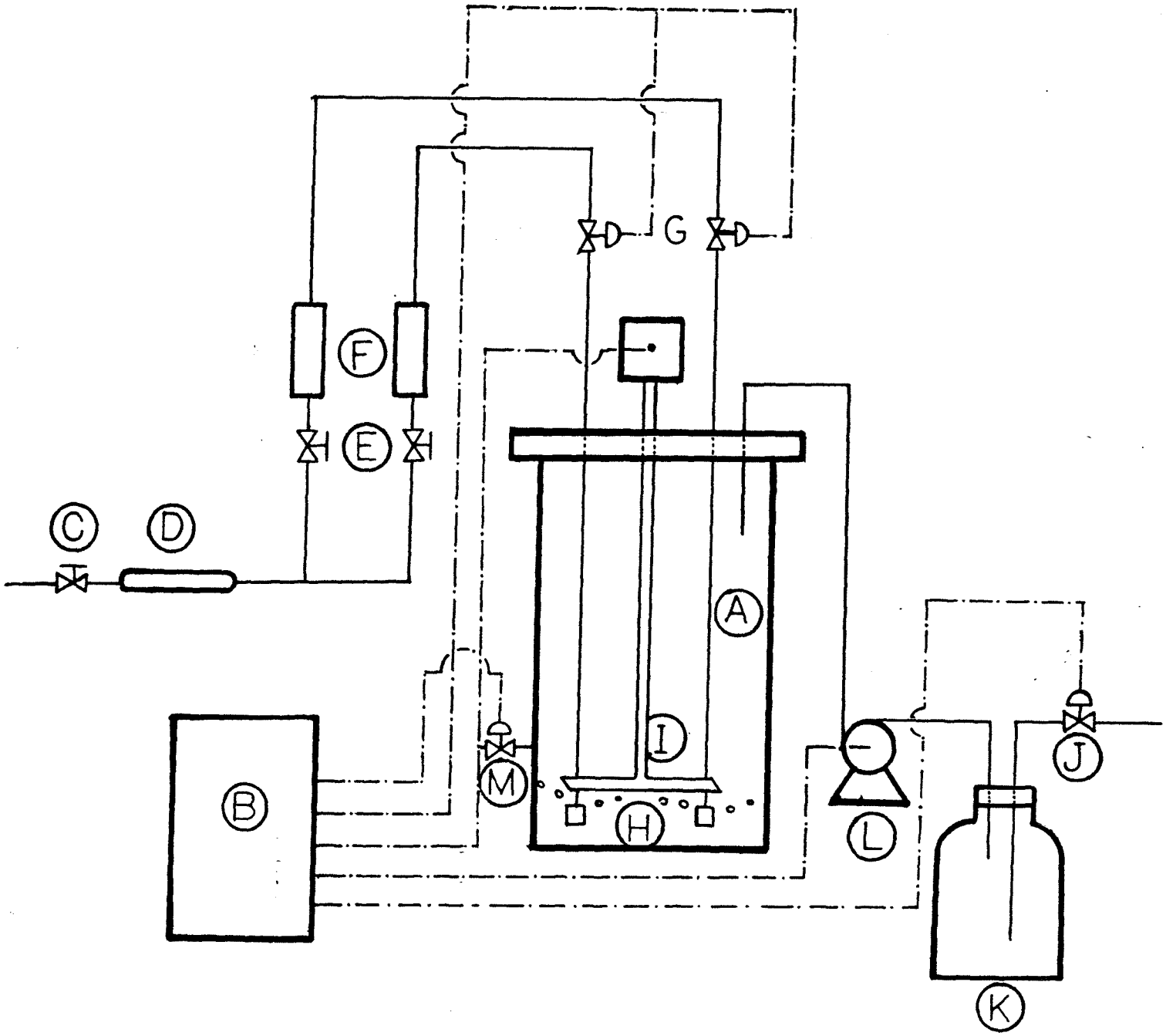
S = Substrate concentration at time t (ppm)
So = Initial substrate concentration (ppm)
K = Zero order kinetic rate constant (ppm/hr)
t = Time (hr)

Substrate	Experiment	Cycle	Rate Constant (K)
Phenol	I	1	12.258
		3	57.515
		4	50.747
		9	56.953
	II	4	58.056
	III	4	75.875
	VIII	4	75.137
		9	95.992

Table # 11 Continued

Substrate	Experiment	Cycle	Rate Constant (K)
2-Chlorophenol	III	9	0.2605
	IV	4	0.1923
	V	4	0.1168
		8	0.0382
		12	0.1392
	VI	8	0.5075
	VII	8	1.3608
		12	1.4154
	VIII	13	3.4943

Figure #1 Schematic of Fill-and-Draw Reactor



A. Reactor
B. Microprocessor
C. Main Valve
D. Air Filter
E. Rotameter Control
F. Rotameter
G. Air Solenoid Valves
H. Diffuser Stone
I. Mixer
J. Feed Solenoid Valve
K. Feed Bottle
L. Influent Pump
M. Decant Solenoid Valve

Figure #2 Phenol Concentration in React Phase of Experiment I
Cycle 1 (Feed 2-hr, React 5.5-hr)

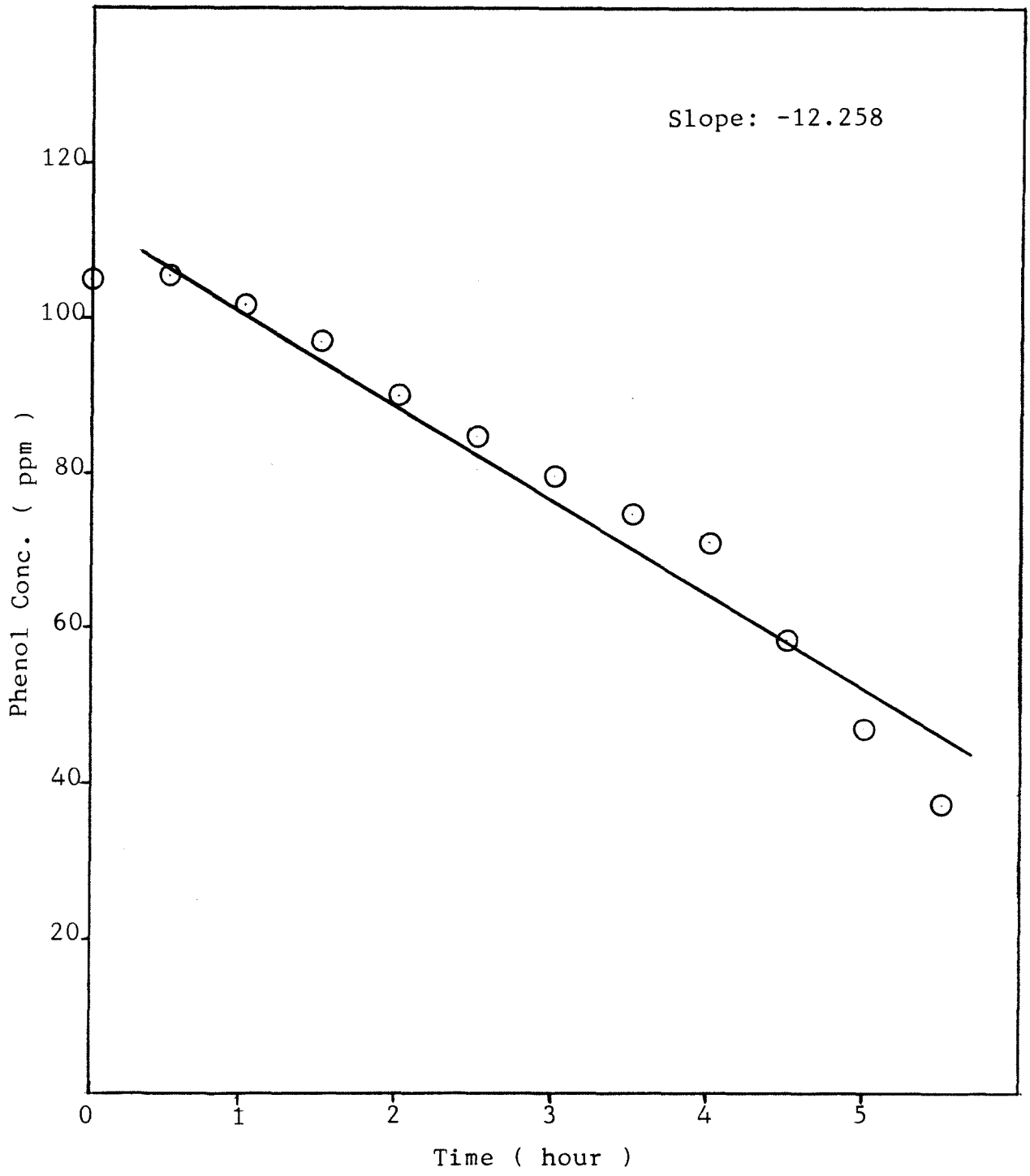
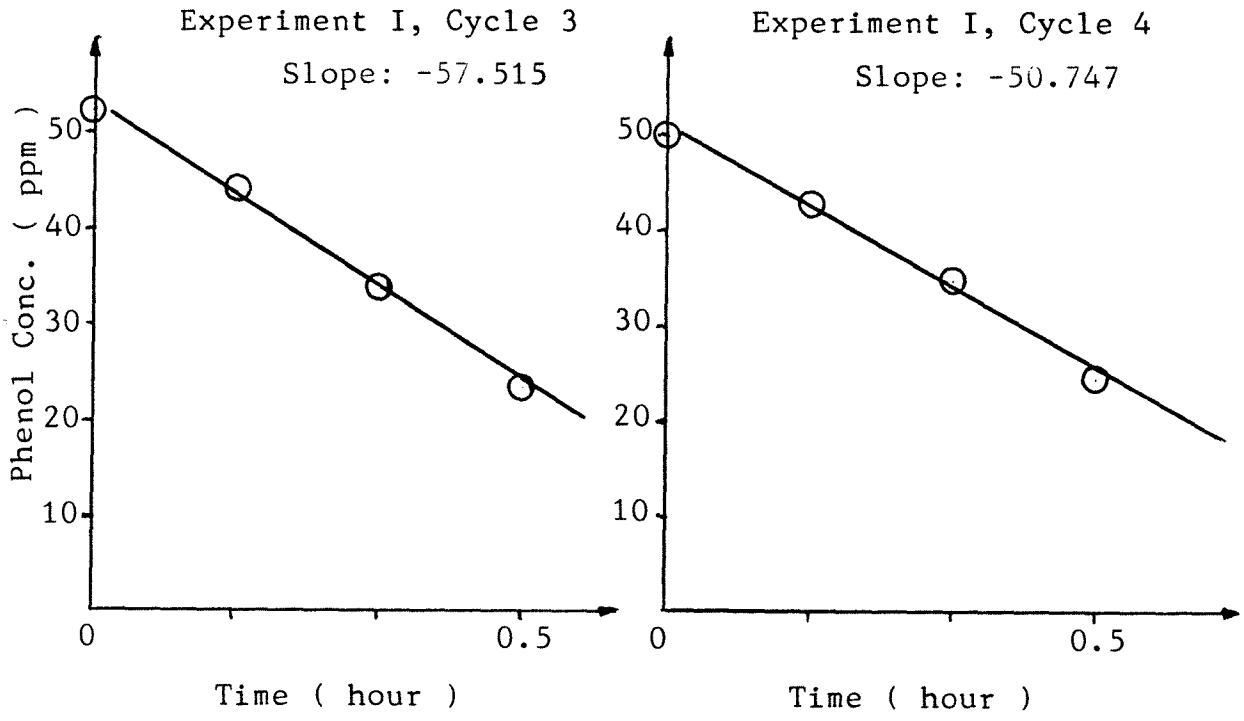
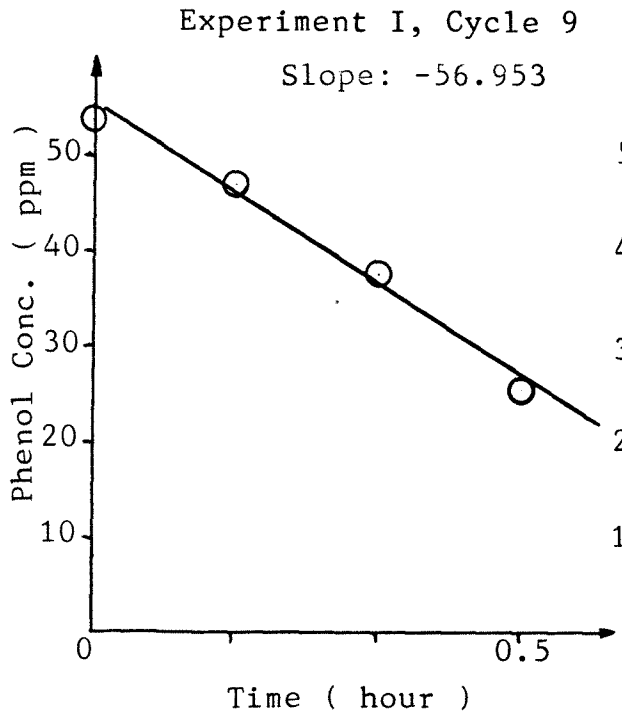


Figure #3 Phenol Concentration in React Phase
(Feed 2-hr, React 5.5-hr)





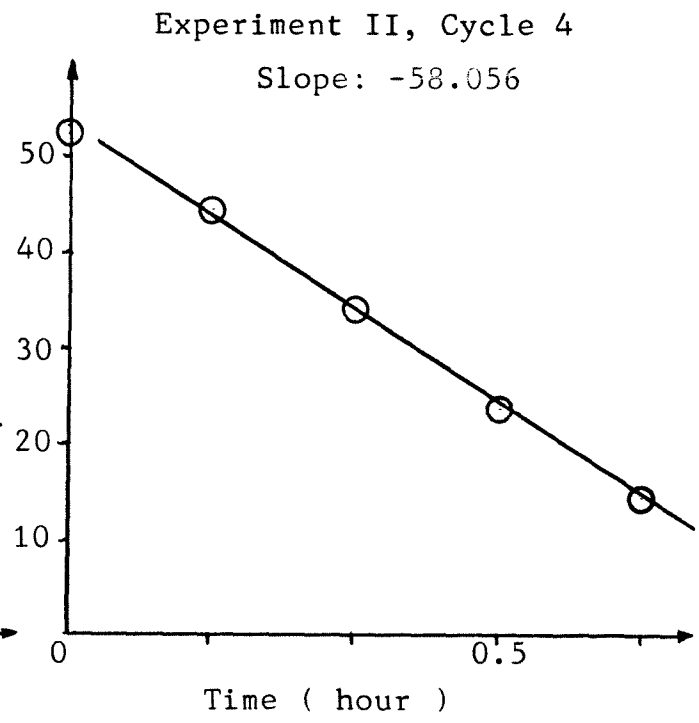


Figure #4 Phenol and DO Concentration in React Phase of Experiment III Cycle 4
(Feed 2-hr, React 5.5-hr)

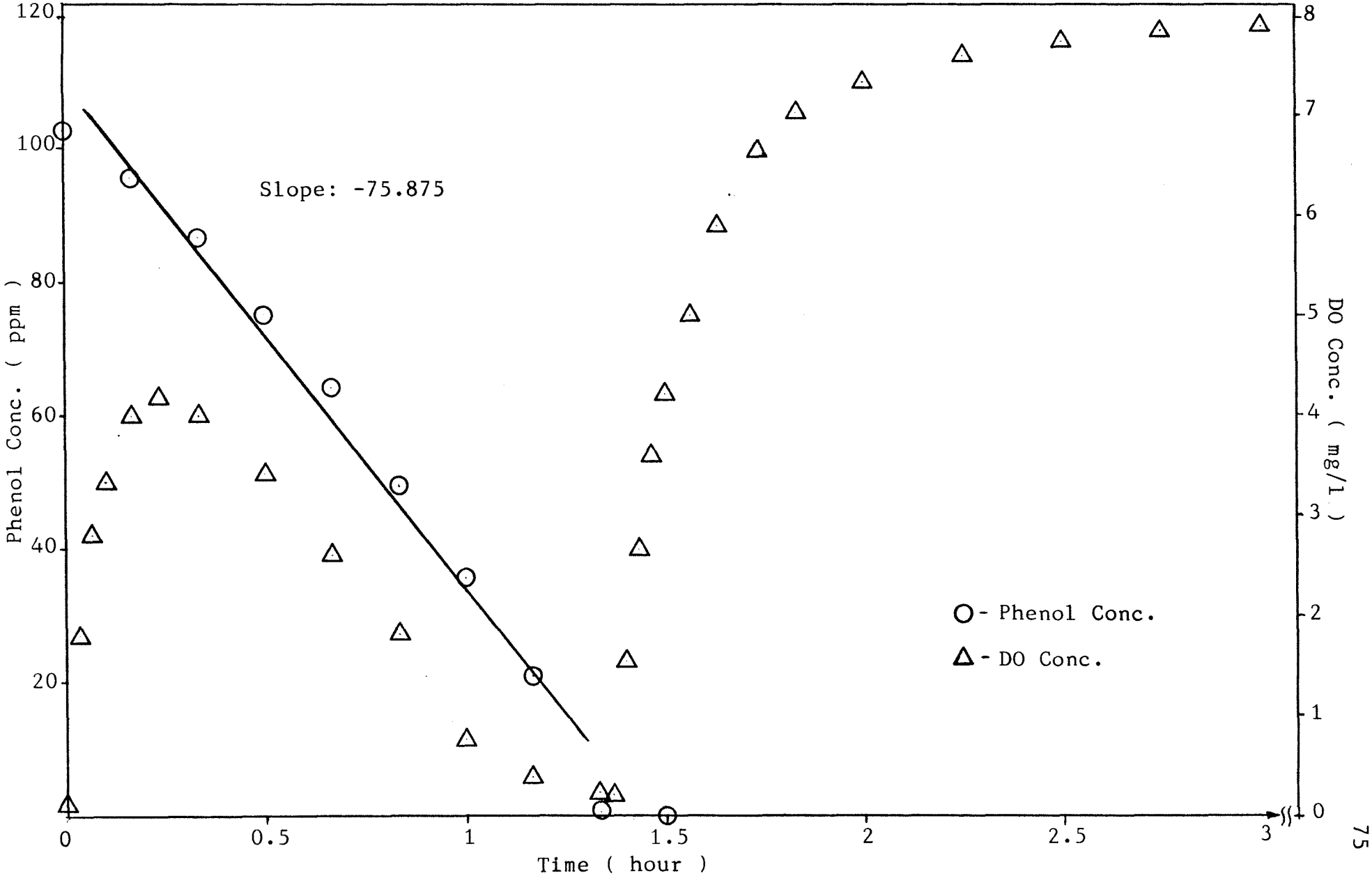


Figure #5 2-chlorophenol and DO Concentration in React Phase of Experiment III
Cycle 9 (Feed 2-hr, React 5.5-hr)

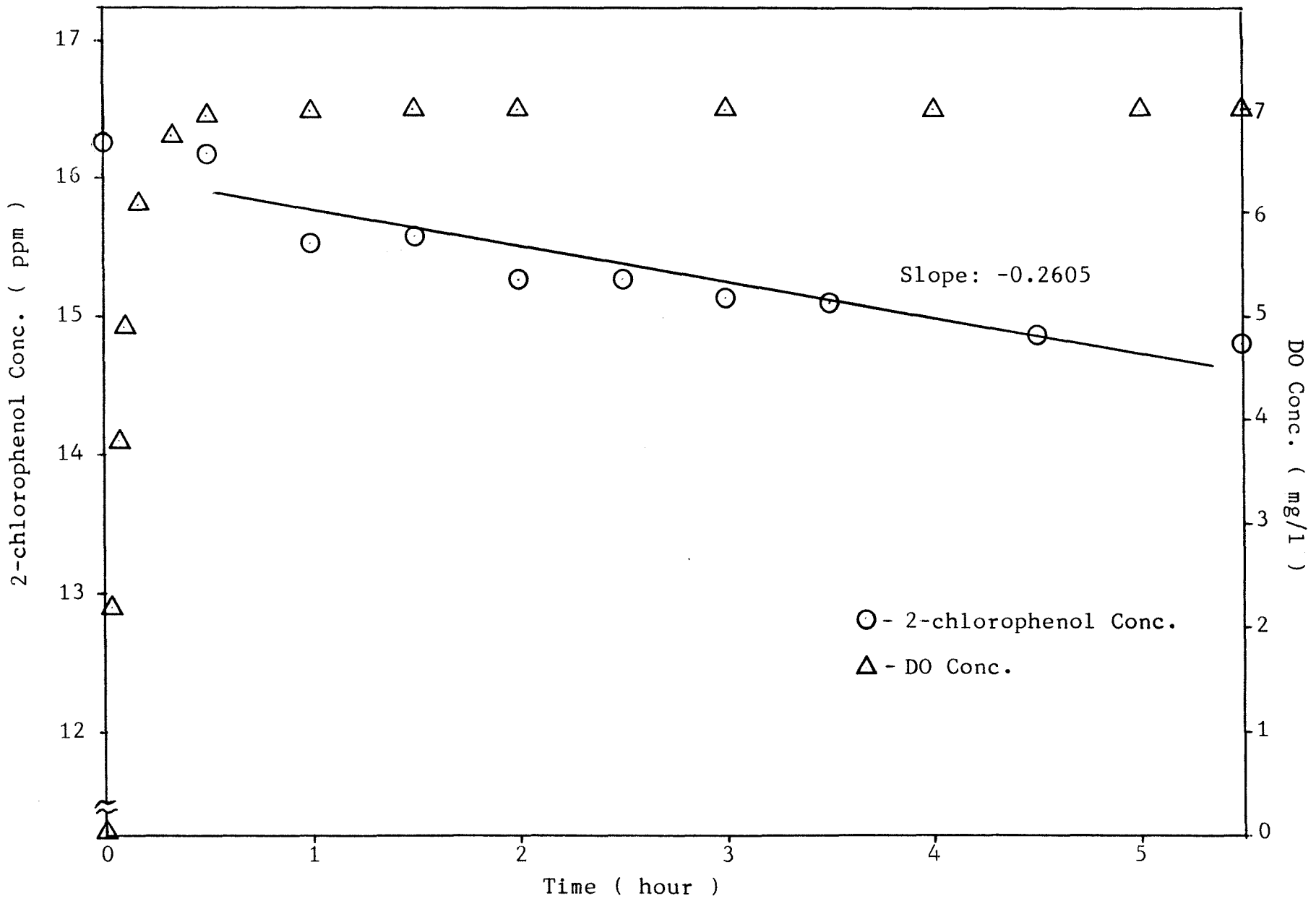


Figure #6 2-chlorophenol and DO Concentration in React Phase of Experiment IV Cycle 4 (Feed 2-hr, React 5.5-hr)

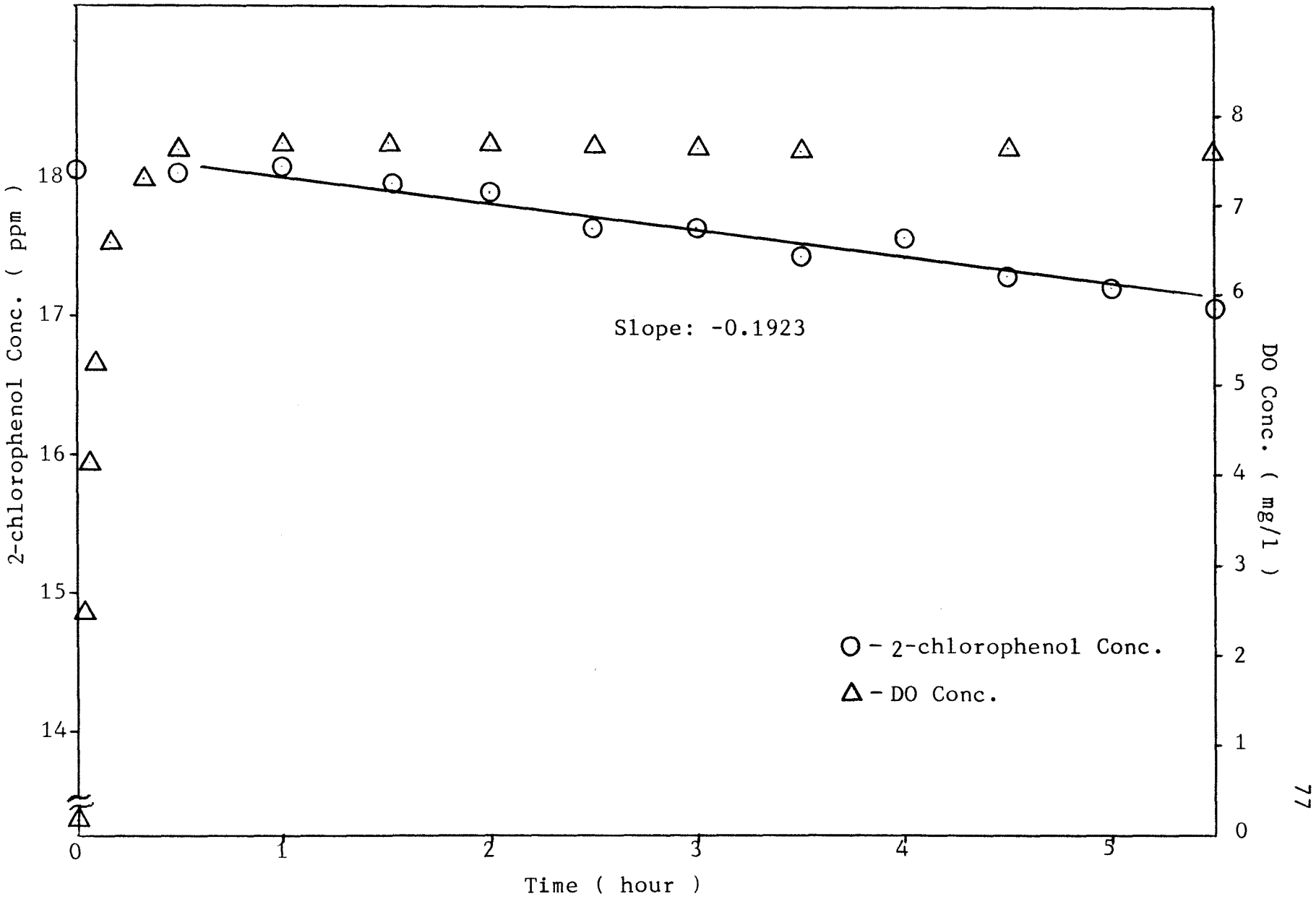


Figure #7 2-chlorophenol Concentration in React Phase of Experiment V (Feed 0.5-hr, React 11-hr)

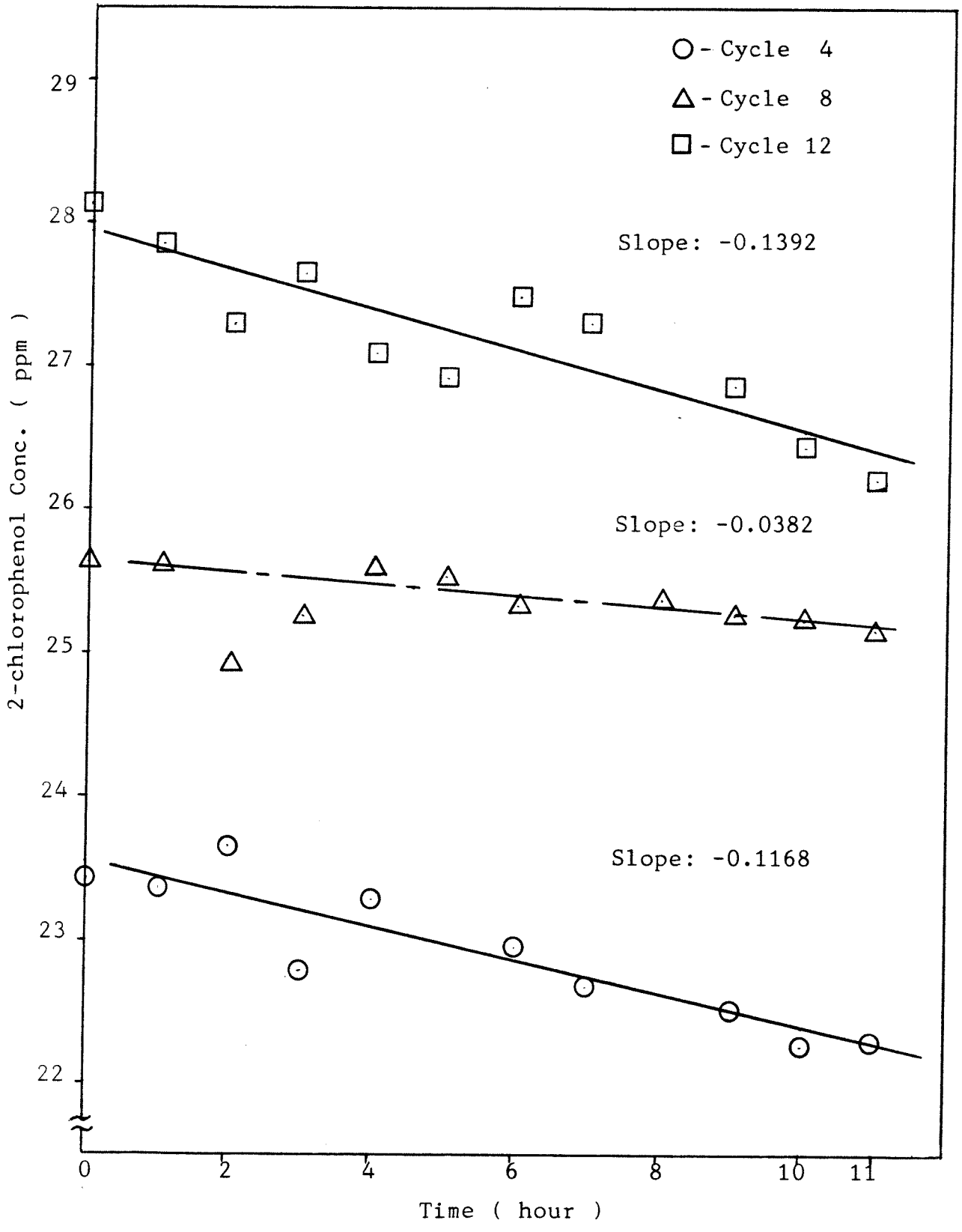


Figure #8 2-chlorophenol and DO Concentration in React Phase of Experiment VI
Cycle 8 (Feed 0.5-hr, React 11-hr)

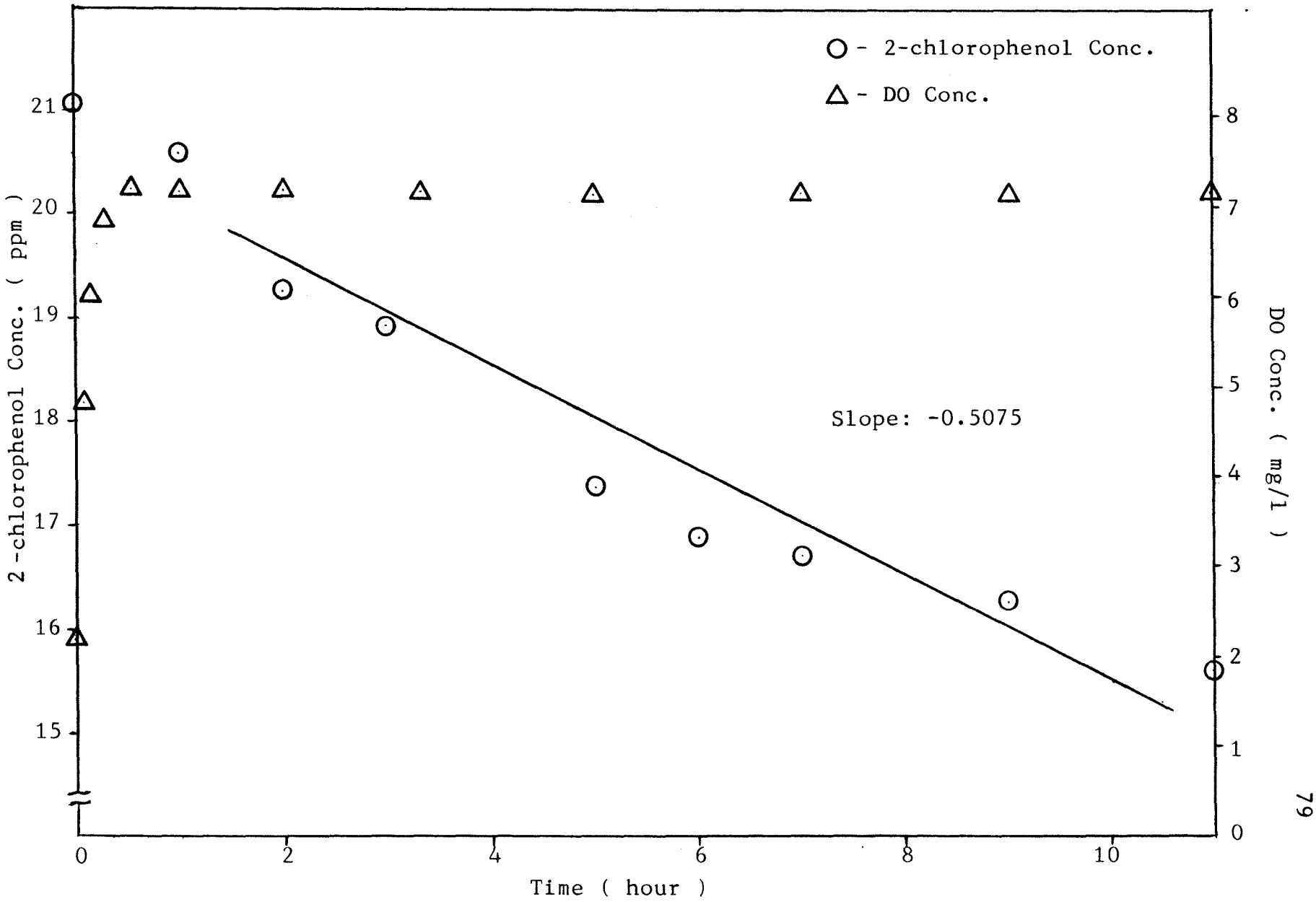


Figure #9 2-chlorophenol and DO Concentration in React Phase of Experiment VII
Cycle 8 & Cycle 12 (Feed 0.5-hr, React 11-hr)

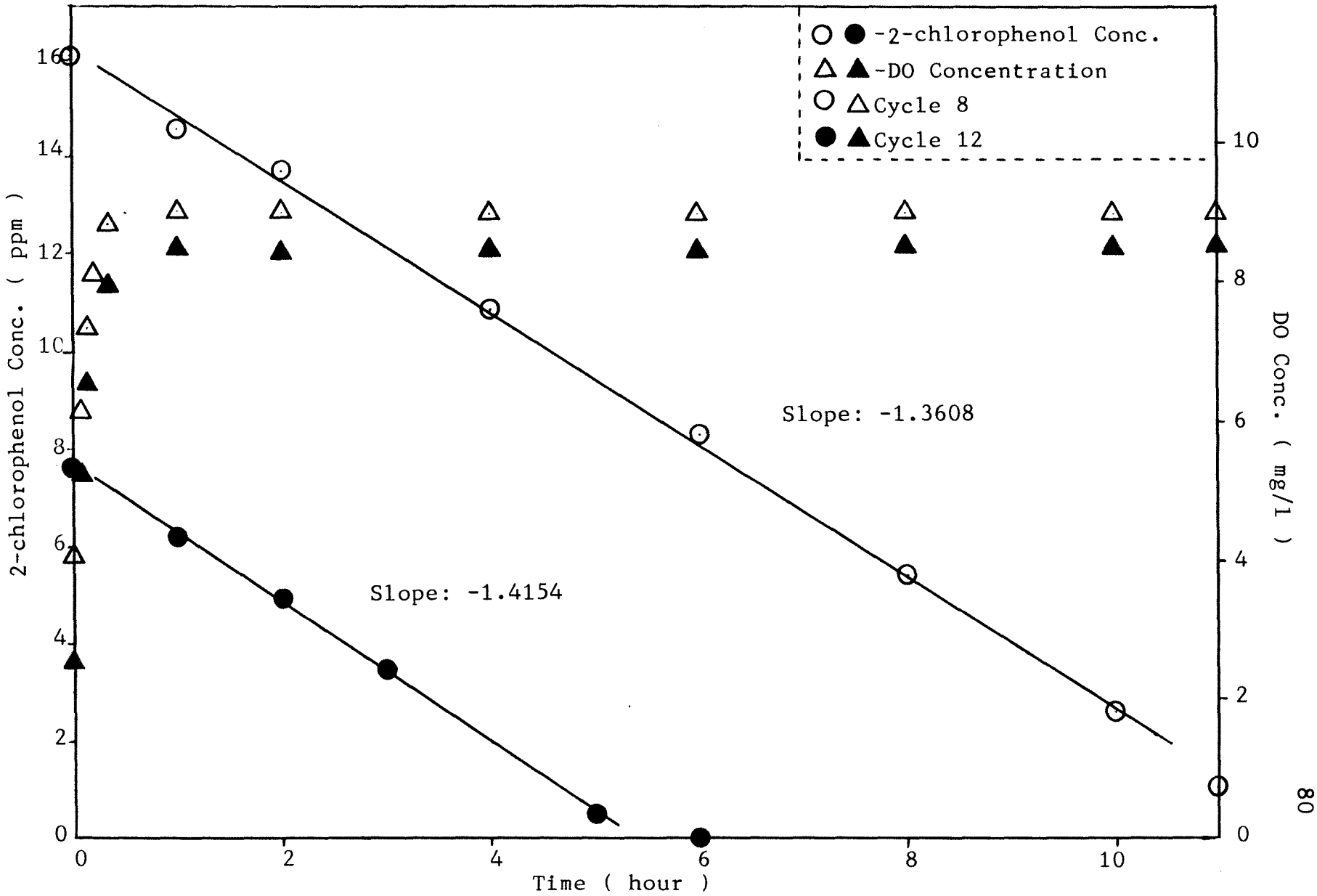


Figure #10 Phenol and DO Concentration in React Phase of Experiment VIII Cycle 4
(Feed 2-hr, React 5.5-hr)

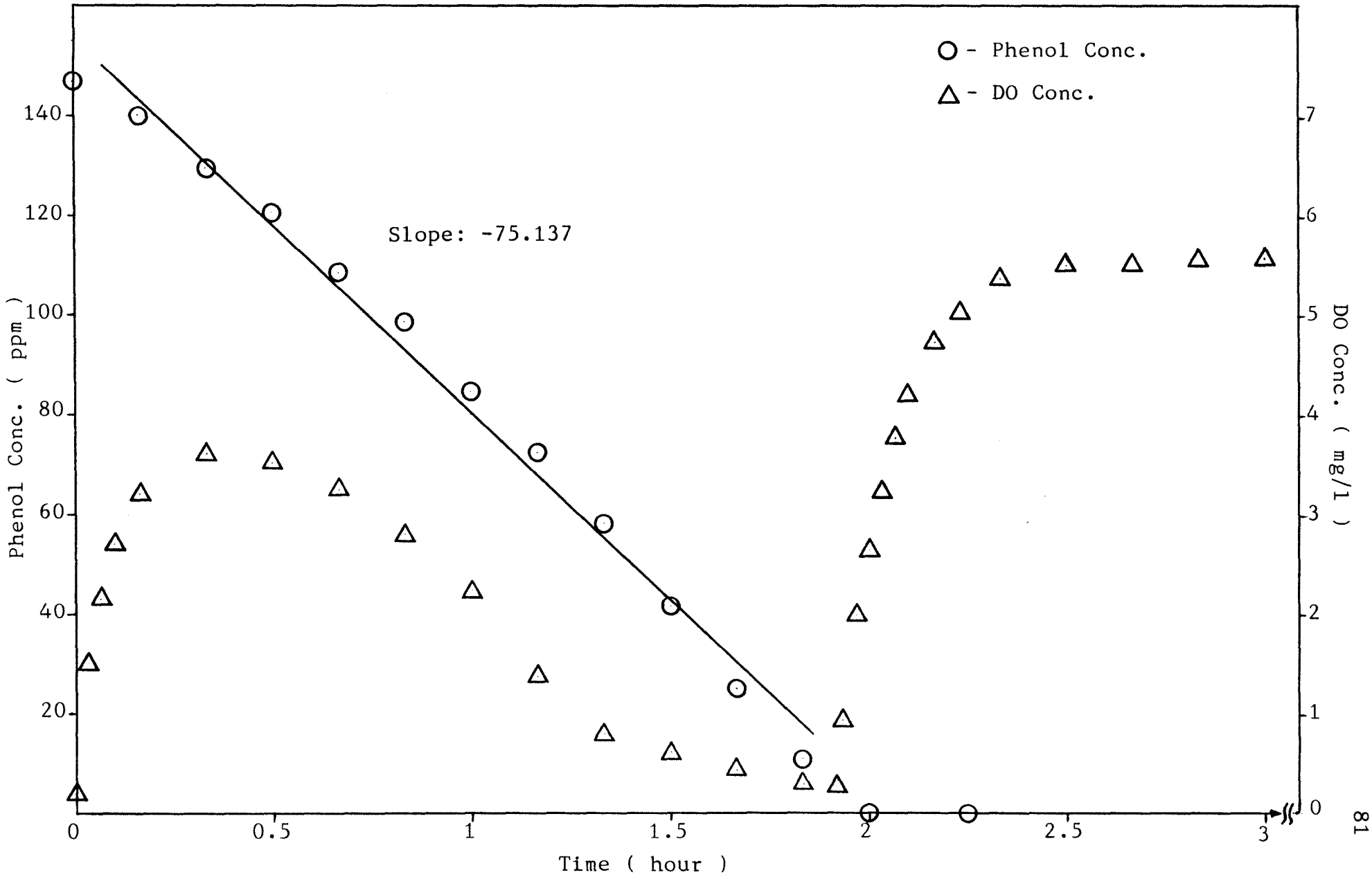


Figure #11 Phenol and DO Concentration in React Phase of Experiment VIII Cycle 9 (Feed 0.5-hr, React 2-hr)

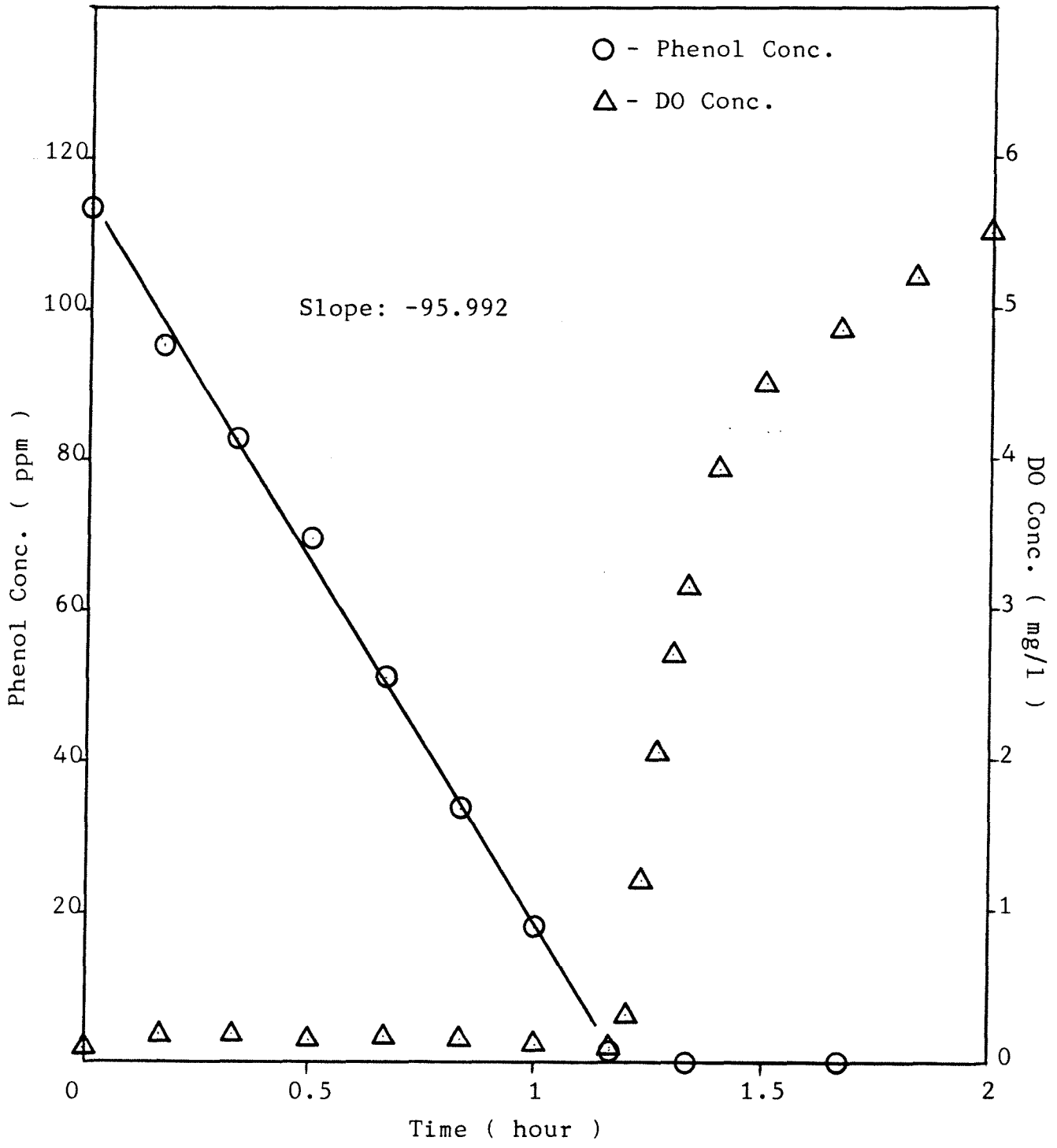


Figure #12 2-chlorophenol and DO Concentration in React Phase of Experiment VIII Cycle 13
(Feed 0.5-hr, React 11-hr)

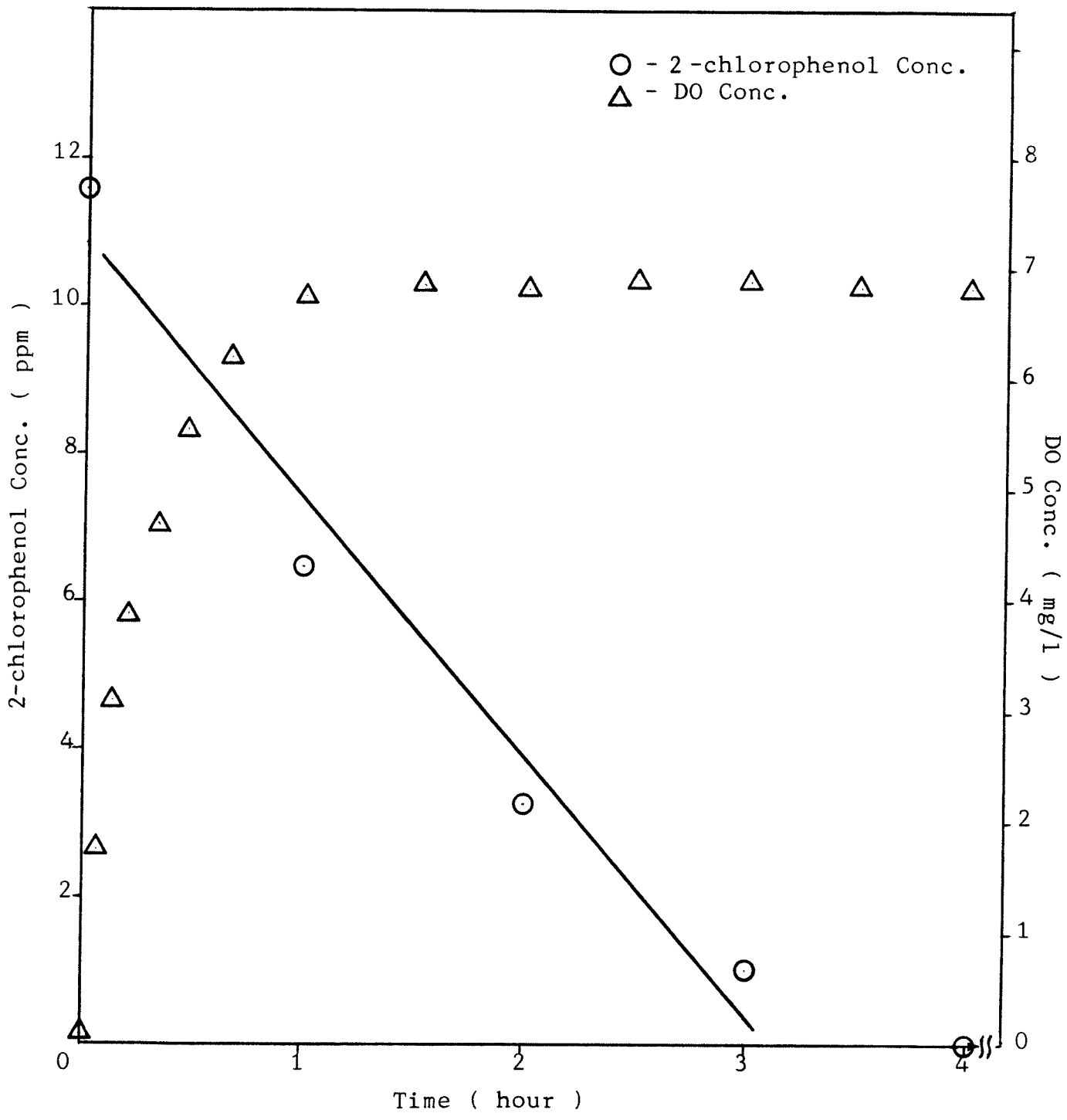


Figure #13 pH and DO in Experiment VIII Cycle 13 (Feed 0.5-hr, React 11-hr
Substrate: 2-chlorophenol)

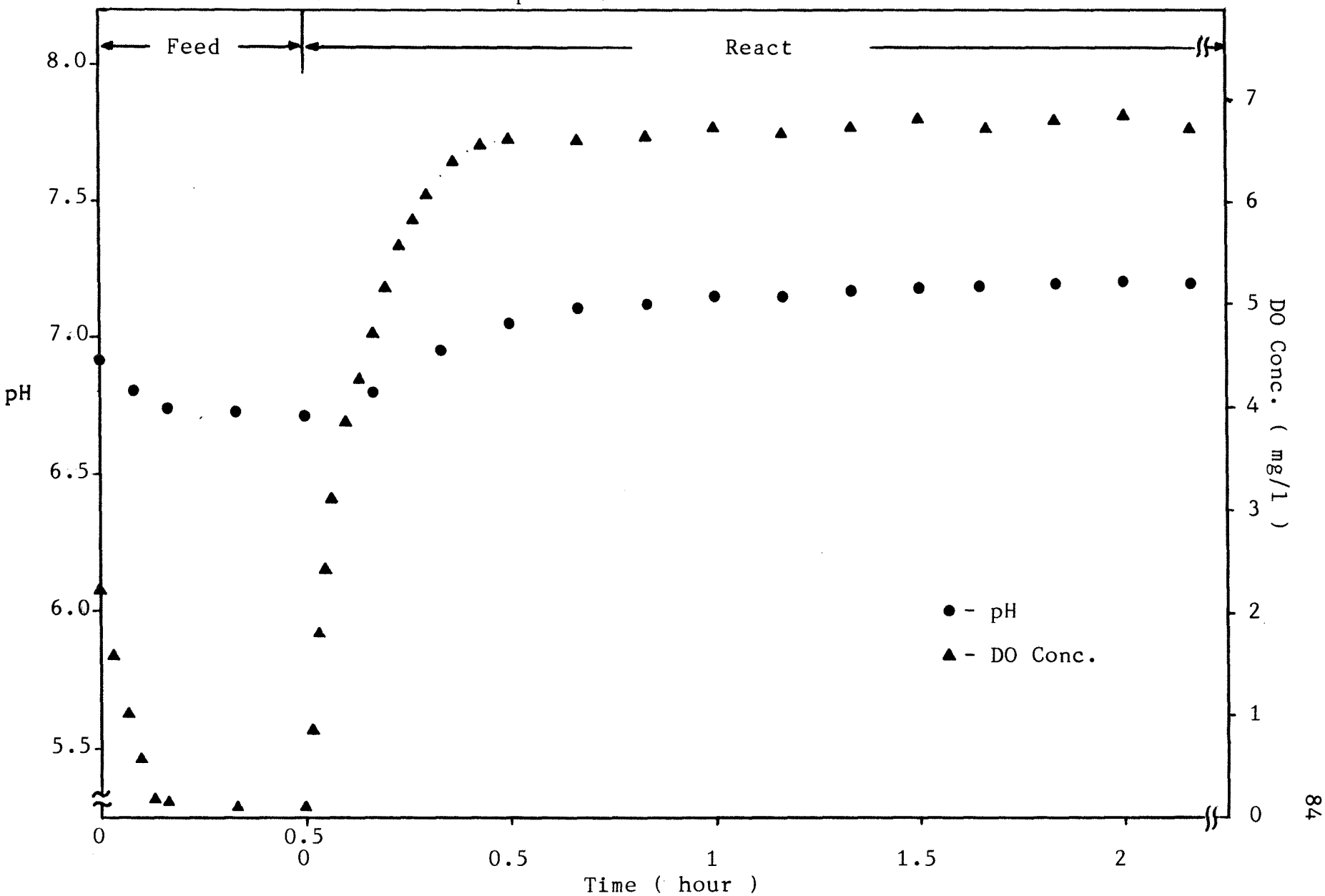


Figure #14 pH, DO, and Phenol Concentration in Experiment VIII Cycle 4
(Feed 2-hr, React 5.5-hr)